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VOLUME IX (1954)

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A CRYOSCOPIC METHOD FOR THE DETERMINATION OF THE TOTAL AMOUNT OF ARENES (AROMATIC HYDROCARBONS) AND UNSATURATED HYDROCARBONS IN KEROSENE AND GAS-OIL PETROLEUM FRACTIONS

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In a previous article [1], we described in detail a cryoscopic method which we had worked out for the quantitative determination of arenes in ligroin, kerosene, and gas-oil petroleum fractions from straight run distillation, i.e., in fractions which do not contain unsaturated hydrocarbons. The aim of the present work is to apply the cryoscopic method to the determination of the total content of arenes and unsaturated hydrocarbons in hydrocarbon mixtures containing unsaturated hydrocarbons, in particular in cracked products

The difficulty of determining aromatic hydrocarbons and unsaturated hydrocarbons is attributable to the fact that unsaturated hydrocarbons are hardly touched on treatment with sulfuric acid, and remain for the most part in the hydrocarbon layer as polymers Attempts to get a complete absorption of unsaturated hydrocarbons with sulfuric acid by changing the conditions of treatment did not give positive results. Only when a 14% solution of phosphorus pentoxide in 100% sulfuric acid was used (30 g phosphorus pentoxide in 100 ml 100% sulfuric acid) were the arenes and unsaturated hydrocarbons completely absorbed. Thus, the use of a 14% solution of phosphorus pentoxide in 100% sulfuric acid enables the cryoscopic method to be applied not only for the determination of arenes but for the total amount of arenes and unsaturated hydrocarbons.

The cryoscopic method of determining the total amount of arenes and unsaturated hydrocarbons is briefly as follows. 10-13 ml of cyclohexane is introduced into the inner tube of a Beckman molecular weight apparatus and its initial crystallization temperature determined. 3-5% (mol) (0.3-0.5 ml) of the test material is then added to this amount of cyclohexane and the initial crystallization temperature determined again. In order to remove the arenes and unsaturated hydrocarbons, the solution is heated with one volume of a solution of phosphorus pentoxide in sulfuric acid, after which it is separated from the acid tarry residue, washed successively with water, 10% sodium hydroxide, then again with water until a neutral reaction is obtained; it is finally dehydrated with anhydrous calcium chloride. The initial temperature of crystallization is then determined once again for the solution after the above treatment.

The total content of arenes and unsaturated hydrocarbons can be calculated by means of the equation:

$$x = 100 \cdot \frac{\Delta t_2}{\Delta t_1}, \qquad (1)$$

where x is the content of arenes + unsaturated hydrocarbons, in mol %; Δt_1 - the depression of the crystallization temperature of cyclohexane on addition of the test mixture; Δt_2 - the elevation of the crystallization temperature of the cyclohexane solution of the test mixture after removal of arenes and unsaturated hydrocarbons by treatment with a sulfuric acid solution of phosphorus pentoxide, in degrees Centigrade.

Properties of the Original Materials and General Experimental Technique.

The properties of the materials not described in [1] are included in Table 1.

TABLE 1

Properties of the original individual hydrocarbons and mixtures of hydrocarbons.

Name of hydrocarbon	Molecular weight	$t_{cryst.}$ °C	Distillation range at 760 mm, in °C	n_D^{20}	Content of unsulfonatable material, mol. %	Iodine Number MacIlliny	Content of unsaturated hydrocarbons, mol. % 1)	Critical solution temperature in aniline, °C
Caprylene	-	-	122-123	1.4139	-	221.1	97.5	-
1-Nonene	-	-	142-144	1.4161	-	199.5	99.0	-
Triisobutene	-	-	160-193	1.4410	-	-	96.0	-
1-Heneicosene	-	33.4	-	-	-	-	-	-
Arenes, isolated from Baku petroleum.....	140.1	-	167-291	1.5320	1.7	-	-	-
Alkanes and cyclanes from Baku ligroin.....	137.0	-	150-200	1.4330	-	-	-	63.2

1) Calculated on the basis of the iodine number.

The properties of the other hydrocarbons which are not included in Table 1 were given in Table 1 of the previous article [1]. The percentages of unsulfonatable matter in the original arenes as found by the cryoscopic method were as follows: 1-methylnaphthalene - 1.1%; triethylbenzene - 1.0%; 2,6-dimethylnaphthalene - 1.3%; and diamylnaphthalene - 0.7% (mol.).

The mixtures of alkanes and cyclanes included in Table 1 were prepared by treating the respective petroleum fractions with 99% sulfuric acid until there was no change in the cryoscopic constant. Caprylene (a mixture of 1 and 2-octenes) was prepared by the dehyration of secondary octyl alcohol over aluminum oxide; 1-nonene was isolated from the products of cracked paraffin by a method described in [2]. In order to ensure freedom from possible contamination by polymerization products, the original alkenes were distilled just prior to their use for making up the synthetic mixtures.

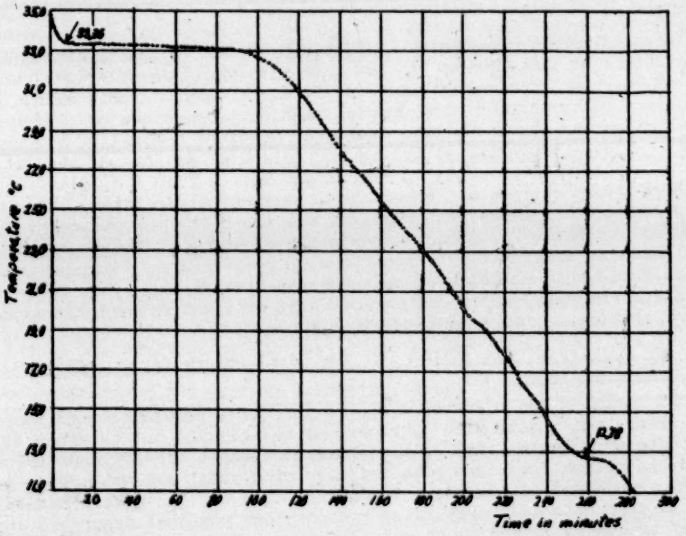
1-Heneicosene which was synthesized in Moscow University by I.I. Tits-Skvortsov by the reaction of allyl bromide with magnesium octadecylbromide was purified further by 3 successive crystallizations from toluene, and two recry-

stallizations from dichloroethane, followed by fractional distillation under a reduced pressure of 2-3 mm Hg from a flask fitted with a column filled with wire spirals. The take off height was 14 cm. The first fraction (crystallization temperature 33.2°) and residue (crystallization temperature 50°) were rejected. The remaining 4 fractions (crystallization temperature 33.3-33.4°), which represented a 76.9% yield from the original hydrocarbon, were combined.

In order to prepare the purified 1-heneicosene as described above, a cooling curve was plotted using an apparatus for molecular weight determination by the cryoscopic method (see diagram). A constant difference of 2° was maintained between the temperature of the 1-heneicosene and that of the cooling bath. The temperature of the heneicosene was determined on a normal thermometer with scale divisions of 0.1°. Readings to hundreths of a degree were made with the help of a magnifying glass.

On the basis of the cooling curve (see diagram) we found that the initial crystallization temperature of the 1-heneicosene which we prepared was 33.36°. The crystallization temperature depression at the 50% mark ($\Delta t_{50\%}$) was 0.06°. From this we calculated that [3], the crystallization temperature of 100% 1-heneicosene should be 33.42°. It also follows from the cooling curve that a transformation occurs in the crystalline phase at 12.78°, i.e. roughly around the 12.8° mark. A mixture of 95.8% (mol.) 1-heneicosene and 4.2% (mol.) cyclohexylcyclohexane has a crystallization temperature which is 0.76 ± 0.02° lower than that of the original 1-heneicosene.

Consequently, 1% (mol.) of solute leads to a depression of the crystallization temperature of 1-heneicosene of 0.181 ± 0.005°, or the cryoscopic constant (A) of 1-heneicosene is equal to 5.5 mol. % per degree. By means of these results it is possible to calculate that the 1-heneicosene prepared contains (0.06/0.181) = 0.3% mol of some other material, in other words the purity of the 1-heneicosene is 99.7% (mol). Refractive index was determined on an Abbe refractometer, critical solution temperature in aniline by the GrozNII method [4], and molec-



ular weights cryoscopically in benzene.

Removability of Unsaturated Hydrocarbons by Sulfuric Acid and by a Solution of Phosphorus Pentoxide in 100% Sulfuric Acid

The first requirement was the determination of the optimal conditions for complete removal of arenes and unsaturated hydrocarbons from their mixtures with alkanes and cyclanes. Experiments 1-11 (Table 2) were treatments of cyclohexane solutions of alkenes alone, or alkenes mixed with arenes, with sulfuric acid under various conditions. Despite the use of various conditions (lowering the working temperature to 6°, treatment with fuming sulfuric acid, successive treatment with 80, 90, and 100% sulfuric acid), complete removal of unsaturated hydrocarbons was not achieved. The content of the latter (in mol.%) decreased on an average by approximately 50%. There was a greater decrease in the percentage of alkenes; a decrease to 35-14% (mol.), however, was only observed when fuming sulfuric acid was used, but even in this case the unsaturated hydrocarbons were far from fully removed. In addition, the use of fuming sulfuric acid is undesirable in the given instance, because it reacts with alkanes and cyclanes.

It should be noted that decreases in the amount of unsaturated hydrocarbons in the cyclohexane solution, adduced in the last column of Table 2, are expressed in mol. percentages and do not mean a corresponding decrease in the content of unsaturated hydrocarbons expressed as percent weight. Thus, e.g., if the test alkenes contained in the cyclohexane are subjected, as a result of sulfuric acid treatment, only to a dimerization reaction and remain completely in solution in the cyclohexane, then their content expressed as mol. percentage will be halved as a consequence of the doubling of their molecular weight. On the basis of the results of Experiments Nos. 1-11 (Table 2) it is possible to conclude that on treating unsaturated hydrocarbons, or their mixtures with arenes, in a cyclohexane solution with 100% sulfuric acid, the greater part only dimerizes and remains in solution in the cyclohexane. It is clear, therefore, that in order to remove unsaturated hydrocarbons or their mixtures with arenes, sulfuric acid as such is not suitable.

The results of Experiments 12-19 (Table 2) refer to the treatment of cyclohexane solutions of the alkenes (in one case with addition of arenes) with a solution of 30 g phosphorus pentoxide in 100 ml of 100% sulfuric acid. In all cases complete restoration of the crystallization temperature of cyclohexane to its normal value was observed; this indicates complete removal of the unsaturated hydrocarbons, though the structure and molecular weights of the latter varied within wide limits. Only in Experiment No. 12 (Table 2) did 0.02% remain from 5.50% original caprylene. When this experiment was repeated using a longer time for shaking the mixture (20 minutes) all the caprylene was removed (see Experiment No. 13, Table 2). These experiments showed that for a content of 0.2-0.4% (mol.) of unsaturated hydrocarbons in cyclohexane, 5 minutes shaking with the sulfuric acid solution of phosphorus pentoxide was sufficient for their complete removal. For a content of 5-15% of unsaturated hydrocarbons the time of shaking is increased to 20-30 minutes.

Checking the Cryoscopic Method for the Total Determination of Arenes and Unsaturated Hydrocarbons

A final check of the cryoscopic method for the determination of the total amount of arenes and unsaturated hydrocarbons was carried out on synthetic mixtures of these components, viz: 1) a mixture of alkenes and cyclanes prepared by treating petroleum fractions with sulfuric acid until all the arenes had been removed, 2) arenes and 3) alkenes. The method used for the determination of the total amount of arenes and unsaturated hydrocarbons was that described above. The time of treatment in all cases was 5 minutes. The results are given in Table 3.

TABLE 2

Removal of alkenes and their mixtures with diethylbenzene on treatment with one volume of sulfuric acid under various conditions

Expt. No.	Alkenes	Mol.% in cyclohexane		Conditions of treatment with sulfuric acid			Δt_1 [1] (in degrees)	Amount of unsaturates remaining in the cyclohexane (mol.%)	Decrease in the amount of alkenes, in mol. %	
		Alkene	Diethylbenzene	Acid	Duration of treatment (min)	Temperature of treatment (°C)			Absolute %	Relative %
1	Caprylene	26.3	0.0	100% H_2SO_4 [2]	30	20	24.05	9.9	16.4	62
2	same	0.22	0.0	100% H_2SO_4	30	20	0.20	0.08	0.14	64
3	same	0.22	0.0	same	30	6	0.30	0.12	0.10	45
4	same	0.11	0.0	same	30	20	0.10	0.04	0.07	64
5	same	0.22	0.0	80, 90, 100 % H_2SO_4 [3]	30	20	0.27	0.11	0.11	50
6	same	0.22	1.20	100% H_2SO_4	30	20	0.22	0.09	0.13	59
7	same	0.20	1.27	same	30	20	0.33	0.14	0.06	30
8	same	0.22	0.0	0.3% free SO_3	30	20	0.08	0.03	0.19	86
9	same	0.20	1.30	same	30	20	0.17	0.07	0.13	65
10	Triisobutene	1.22	0.0	100% H_2SO_4	30	20	1.68	0.69	0.53	43
11	1-Heneicosene	0.36	0.0	same	30	20	0.25	0.10	0.26	72
12	Caprylene	5.50	0.0	100% H_2SO_4 + $+P_2O_5$ [4]	10	20	0.06	0.02	5.48	99.6
13	same	5.50	0.0	same	20	20	0.00	0.00	5.50	100
14	same	0.22	0.0	same	30	20	0.00	0.00	0.22	100
15	same	0.22	0.0	same	5	20	0.00	0.00	0.22	100
16	same	0.23	1.44	same	5	20	0.00	0.00	0.23	100
17	same	0.15	0.0	same	5	20	0.00	0.00	0.15	100
18	1-Nonene	15.4	0.0	same	30	20	0.08	0.03	15.37	99.8
19	Triisobutene	1.34	0.0	same	5	20	0.00	0.00	1.34	100

1) The difference between the crystallization temperature of the original cyclohexane and of the solution of the test hydrocarbons in the cyclohexane after sulfuric acid treatment. By dividing the values of Δt by 2.42 we can find the amount of contaminant (in mol. %) remaining in the cyclohexane.

2) 3 volumes of sulfuric acid were used in Experiment 1.

3) Successive treatment with 80% and 90% H_2SO_4, one volume of acid each time.

4) A solution of 30 g phosphorus pentoxide in 100 ml 100% sulfuric acid.

TABLE 3

Check on the cryoscopic method for the quantitative determination of total arenes plus unsaturated hydrocarbons in synthetic mixtures. Conditions: 1 volume of 14% (weight) P_2O_5 in 100% H_2SO_4; time of treatment - 5 minutes at 20°.

Expt.No.	Designation of hydrocarbons		Composition of synthetic mixtures in mol. %				
	alkanes and cyclanes[1] fractions in °C	arenes	alkenes	alkanes, cyclanes	arenes	alkenes	
20	150-200	-	-	100.0	-	-	
21	300-350	-	-	100.0	-	-	
22	150-200	-	1-nonene	86.7	-	13.3	
23	150-200	-	1-nonene	78.4	-	21.6	
24	150-200	-	1-nonene	49.8	-	50.2	
25	150-200	diethyl benzene	1-nonene	79.3	10.2	10.5	
26	150-200	ditto	1-nonene	79.3	10.2	10.5	
27	150-200	ditto	1-nonene	79.3	10.2	10.5	
28	150-200	ditto	1-nonene	60.3	20.3	19.4	
29	150-200	ditto	1-nonene	60.3	20.3	19.4	
30	150-200	ditto	1-nonene	60.3	20.3	19.4	
31	150-200	ditto	1-nonene	49.3	9.5	41.2	
32	150-200	ditto	1-nonene	49.3	9.5	41.2	
33	150-200	-	triisobutene	82.8	-	17.2	
34	150-200	arenes fraction 167-291°	-	72.9	27.1	-	
35	150-200	ditto	caprylene	73.1	15.1	2.7	
			1-nonene			3.7	11.8
			triisobutene			5.4	
36	150-200	ditto	caprylene	50.4	29.9	5.1	
			1-nonene			5.4	19.7
			triisobutene			9.5	
37	150-200	ditto	triisobutene	39.1	20.4	9.6	
			caprylene			11.1	40.5
			1-nonene			19.8	
38	300-350	-	1-heneicosene	90.4	-	9.6	
39	300-350	-	1-heneicosene	79.0	-	21.0	
40	300-350	diamyl-naphthalene	-	53.9	46.1	-	
41	300-350	ditto	1-heneicosene	49.0	37.9	13.1	
42	300-350	ditto	1-heneicosene	49.0	37.9	13.1	
43	300-350	ditto	1-heneicosene	49.0	37.9	13.1	

In the previous section it was shown that a solution of phosphorus pentoxide in 100% sulfuric acid removed arenes and unsaturated hydrocarbons from the cyclohexane solution. Before using the reagent, however, it was necessary to confirm that it could not react with the mixture of petroleum alkanes and cyclanes in solution in cyclohexane. If the sulfuric acid solution of phosphorus pentoxide should react with the mixture of alkanes and cyclanes, and the crystallization temperature of their solution in cyclohexane should increase after the sulfuric acid-phosphorus pentoxide treatment, it would mean that the use of this reagent

[1] Petroleum fraction after removal of arenes by treatment with 99% H_2SO_4.

Δt_1 degrees	Δt_2 degrees	Total content of arenes and unsaturated hydrocarbons in mol. %		Deviations, actual minus found, in mol.%	
		Actual	Found	Absolute	Relative
3.74	0.00	0.00	0.00	0.00	0.00
2.24	0.00	0.00	0.00	0.00	0.00
4.5	0.59	13.3	13.1	+0.2	+1.5
2.5	0.55	21.6	22.0	-0.4	-1.9
2.04	1.02	50.2	50.0	+0.2	+0.4
4.10	0.91	20.7	22.2	-1.5	-7.3
3.77	0.79	20.7	21.0	-0.3	-1.4
2.34	0.48	20.7	20.5	+0.2	+1.0
4.24	1.74	39.7	41.0	-1.3	-3.3
4.05	1.61	39.7	39.8	-0.1	-0.3
3.36	1.34	39.7	39.9	-0.2	-0.5
3.78	1.91	50.7	50.5	+0.2	+0.4
3.99	2.02	50.7	50.6	+0.1	+0.2
3.44	0.58	17.2	16.9	+0.3	+1.7
4.22	1.17	27.1	27.7	-0.6	-2.2
3.77	1.00	26.9	26.5	+0.4	+1.5
3.70	1.85	49.6	50.0	-0.4	-0.8
4.70	2.83	60.9	60.2	+0.7	+1.1
1.70	0.17	9.6	10.0	-0.4	-4.2
2.52	0.55	21.0	21.8	-0.8	-3.8
2.69	1.27	46.1	47.2	-1.1	-2.4
2.10	1.01	51.0	48.1	+2.9	+5.7
2.81	1.35	51.0	48.0	+3.0	+5.9
2.75	1.44	51.0	52.4	-1.4	-2.7
		Mean deviation.....		0.7	2.1
		Maximum deviation.....		+3.0	-7.3

would lead to high values for the total amount of arenes and unsaturated hydrocarbons. Experiment (see Expts. Nos. 20 and 21, Table 3) showed that treatment of a mixture of alkanes and cyclanes from 150-200° and 300-350° petroleum fractions, respectively, dissolved in cyclohexane, with the sulfuric acid-phosphorus pentoxide reagent did not affect the crystallization temperature of the cyclohexane solution. This confirms that the sulfuric acid-phosphorus penoxide reagent can be used for the cryoscopic determination of total arenes plus unsaturated hydrocarbons.

This confirms that the sulfuric acid-phosphorus pentoxide reagent can be used for the cryoscopic determination of total arenes plus unsaturated hydrocarbons.

The experimental results (see Experiments Numbers 22-43, Table 3) are completely satisfactory. The mean deviation of the total arenes plus unsaturated hydrocarbons, as determined experimentally, from the actual amount used is equal to to 0.7% absolute and 2.1% relative. The maximum deviation is +3.0% absolute, -7.3% relative.

The results adduced show that the cryoscopic method as developed by the authors of the present article for the determination of total arenes plus unsaturated hydrocarbons is suitable for the analysis of mixtures of hydrocarbons with boiling points roughly between 150-400°.

SUMMARY

1. The crystallization temperature (33.4°) and point of allotropic conversion (12.8°) were determined for a sample of 99.7% pure 1-heneicosene.

2. When solutions of alkenes in cyclohexane were treated with concentrated sulfuric acid the greater part polymerized and remained in the hydrocarbon phase.

3. If instead of sulfuric acid, a solution of phosphorus pentoxide in 100% sulfuric acid is used, polymerization of the alkenes can be avoided and they are completely removed by the acid layer.

4. A method which has been described previously [1], for the quantitative determination of arenes, can be applied also for the determination of total arenes plus unsaturated hydrocarbons in admixture with hydrocarbons boiling in the range 150-400°, if the sulfuric acid used for treatment of the test samples is replaced by a solution of phosphorus pentoxide in 100% sulfuric acid.

5. The mean accuracy of the cryoscopic method for total arenes plus unsaturated hydrocarbons is 0.7% absolute. In all, about 0.5 ml of sample is required.

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THE QUANTITATIVE SPECTROCHEMICAL DETERMINATION OF PRASEODYMIUM IN LANTHANUM AND OF EUROPIUM IN SAMARIUM ON THE ISP-22, A SPECTROGRAPH OF AVERAGE DISPERSION.

G. Kryuger and R.R. Shvangiradze

The determination of small amounts of rare earths in other elements of the same groups and the special interest attached to the preparation of pure members of these groups have recently led research workers to develop various physico-chemical methods of analysis. The best of these methods is quantitative emission spectrum analysis.

In work already published it has been pointed out that the complexity of the spectra of these elements of necessity requires a spectrograph with high resolving power; in America, therefore, grating spectrographs with a focussing distance of 6 m [1,2,3] are used and in Europe spectrographs with high resolving power are also employed [4,5,6].

Table 1 summarizes the latest published results on the quantitative spectrochemical determination of praseodymium in lanthanum and of europium in samarium.

TABLE 1

Published results on the quantitative determination of praseodymium in lanthanum and of europium in samarium

Author	Element determined	Spectrograph	Dispersion in Å/mm	Material of electrode	Form of test and excitation	Analytical lines	Concentration range, in %
Gatterer and Junkes [4]	Eu in Sm	Steinheil f' = 1.6 m	3.2	Graphite	Solution arc = 3.75 A	Eu 4129.74 Å / Sm 4128.1 Å	from 0.005 to 1.0
Fassel and Wilhelm[1]	Eu in Sm	Grating f' =6 m	2.5	Graphite	rare earth oxide + graphite powder 1:1 = arc 17 A	Eu 4129.74 Å / Sm 4129.23 Å	from 0.1 to 2.0
						Eu 4627.12 Å / Sm 4628.79 Å	from 0.01 to 0.2
Fassel, Cook, Krotz Kehres [2]	Pr in La	Grating f' =6 m	2.5	Graphite	rare earth oxide + graphite powder 1:1= arc 17-18 A	Pr 4408.84 Å / La 4393.51 Å	from 0.05 to 1.0

With regard to Gatterer and Junkes method one can say that they considerably increased the sensitivity of the determination of europium in samarium by multiple excitation of the sample in an arc.

Their method of analysis is, however, far more time consuming than normal spectrochemical analysis; their method is therefore not suitable for carrying out large numbers of analyses. On the other hand, the method proposed by Fassel and coworkers is distinguished by the simplicity of the preliminary preparation of the sample (mixing the test sample with graphite powder in the ratio 1:1) and their method of excitation.

All the methods mentioned in Table 1 have the following features in common: the use of a constant current arc between needle electrodes as the source, the choice of a basic element as the internal standard, and the use of spectrographs of high resolving power.

Our problem was to develop a method for the quantitative spectrochemical analysis of mixtures of rare earths with a spectrograph of average dispersion, the ISP-22.

Results are given in this article of quantitative methods of determining praseodymium in lanthanum and of europium in samarium using this apparatus.

Choice of Electrode Material and Spectrum Excitation Source

As pointed out above, the authors mentioned [1,2,4] used a constant current arc between needle electrodes. However, after using a spectrograph with average dispersion we became convinced that the band spectrum of cyanide (CN) seriously interferes in the wave length range we were interested in. We did not use the method proposed by Smith and Wiggins for excluding the cyanide band, viz. arcing in water vapor, since it is unsuitable for carrying out large numbers of determinations. We accordingly chose copper as the material for the electrodes.

When working with copper electrodes it is essential to use an AC arc; for stabilization of the discharge conditions we used an AC arc with high frequency ignition on the Sventitsky plan. Substitution of graphite electrodes by copper ones, apart from eleminating the cyanide bands, has a further advantage: pure copper electrodes are cheaper and more readily available than spectrally pure graphite electrodes.

In order to prevent scattering of test sample from the electrode openings during arcing burning, various fixing agents are used in practice; these also favor evaporation and excitation of test samples in many cases. In our case it was impossible to use organic compounds (appearance of cyanide bands). Potassium bisulfate was therefore chosen ($KHSO_4$), and this was mixed in the ratio of 4:1 with the rare earth oxide (4 parts $KHSO_4$ to 1 part rare earth oxide). The opening in the lower electrode was filled with this mixture, where it was subsequently melted on an electric hot plate until a caked test sample was obtained; this caked material was not then scattered on heating in the arc.

McClelland [6], was the first to use potassium bisulfate as a fixer, though he used it in a somewhat different way; the base in his case was ferric oxide mixed with the rare earth, iron being used as the internal standard. In our case, addition of iron, which has a fairly complicated spectrum, would have led to additional troubles in resolving the spectra

Moreover, in determining rare earths it is more suitable to use as the internal standard a base element of the rare earth mixture. Simply mixing the rare earths with potassium bisulfate gave satisfactory results.

Choice of Analytical Lines and Working Conditions

There are in all four sensitive lines in the spectrum of praseodymium which are free from superposition by lanthanum lines and from interference on the part of the copper electrode. These lines are: Pr II 3908.43 Å; Pr II 3908.03 Å; Pr II 4100.75 Å; Pr 4222.98 Å.

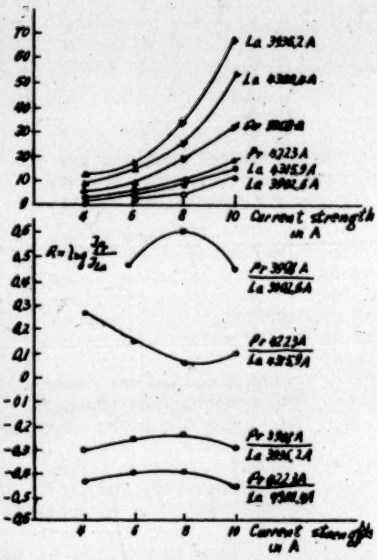

Fig. 1. Relation between absolute and relative intensities of the praseodymium and lanthanum lines, and current strength. (In this and subsequent figures, J = I (intensity).

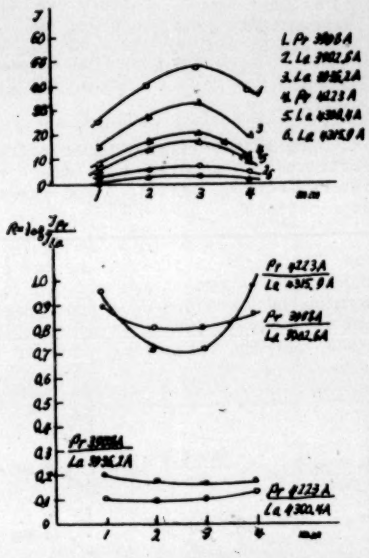

Fig. 2. Relation between absolute and relative line intensities of praseodymium and lanthanum, and inter electrode distances.

The line 4408.84 Å for Pr II which was used by Fassel and coworkers [2], suffers in our case from interference from the 4415.6 Å copper line.

The Pr II lines 3908.43 Å and 3908.03 Å are not resolved by the ISP-22 spectrograph, since its dispersion in the 3900 Å region only amounts to 34 Å/mm. The composite line arbitrarily denoted by us henceforth as Pr II 3908 Å is more intense than either of the lines composing it. For comparison we used the line of the base element La II 3936.22 Å; according to tabulated results it should have superimposed on it Pr 3935.82 Å, but under our conditions at a concentration of up to 10% praseodymium in lanthanum this line did not prove reliable, i.e. the La II 3936.22 Å line is practically free from superposition by the praseodymium line. This assumption is confirmed by the strict straight line shape of the calibration curve (Fig.6).

In order to make a final choice of the analytical lines to be used for praseodymium and lanthanum the following pairs of analytical lines were studied in detail:[1)]

1. $\frac{\text{Pr II 3908 Å}}{\text{La II 3936.2 Å}}$;

2. $\frac{\text{Pr II 3908 Å}}{\text{La I 3902.6 Å}}$;

1) This was part of the work V.L.Dzhiky carried out for his diploma.

3. $\frac{\text{Pr } 4223.0 \text{ Å}}{\text{La II } 4300.4 \text{ Å}}$;

4. $\frac{\text{Pr } 4223.0 \text{ Å}}{\text{La } 4315.90 \text{ Å}}$.

The suitability of these pairs of lines for analytical purposes was investigated by studying the effect of the arc parameters (current strength, inter-electrode distance) and exposure time on their absolute and relative intensities.

The results of these investigations on the relationships between the absolute and relative intensities of the praseodymium and lanthanum lines and current strength are adduced in Fig. 1. Samples containing 3% praseodymium in lanthanum were photographed for an exposure time of 60 seconds, and an inter-electrode distance of 3 mm. The intensity values were determined from the blackening curve of the photographic plate. The background around the line was taken into account. As shown in Fig. 1 all the pairs of lines apart from Pr II 3908 A/La I 3902.6 A [1]) gave satisfactory results. On the basis of this work a current of 9A was chosen for further work, since it was more suitable for the concentration range at which we were working (from 0.3 to 10% Pr in La).

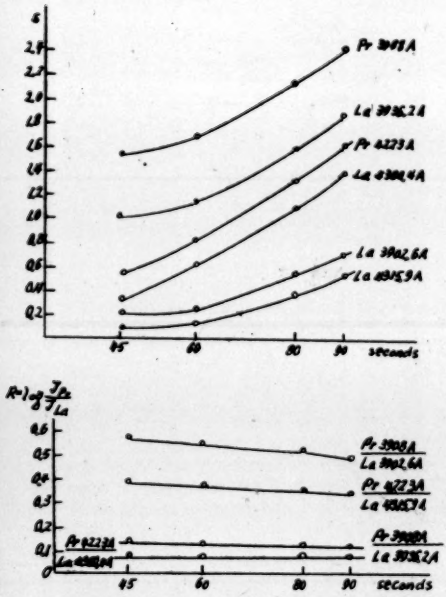

Fig. 3. Variation of the blackening of praseodymium and lanthanum lines and their relative intensities with exposure time.

Results of the study on the relationships between the absolute and relative intensities of the praseodymium and lanthanum lines, and inter-electrode distances are adduced in Fig. 2. The spectra were photographed at a current strength of 9A and an exposure time of 60 seconds. It is clear from Fig. 2 that only two pairs of lines: Pr II 3908 A/La II 3936.2 A and Pr 4223 0 A/La 4300.4 A behave satisfactorily. For further work we chose an interelectrode distance of d = 3 mm. Unstable burning of the arc occurs if this distance is increased.

Using the conditions chosen (current strength 9A, and interelectrode distance d = 3mm)

[1]) This is not surprising in view of the fact that the pair of lines from ionized and neutral atoms always show comparatively greater variations.

the variation of the blackening of praseodymium and lanthanum lines and their relative intensities with exposure time was studied. These results are represented graphically in Fig. 3. All four pairs of lines behave well, particularly Pr 3908 A/La 3936.2 A and Pr 4423 A/La 4300.4 A, the relative intensities of which remain completely unchanged with exposure time.

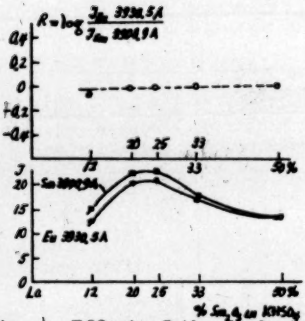

Fig. 4. Effect of the Sm_2O_3 to $KHSO_4$ ratio on the absolute and relative intensities of the samarium and europium lines.

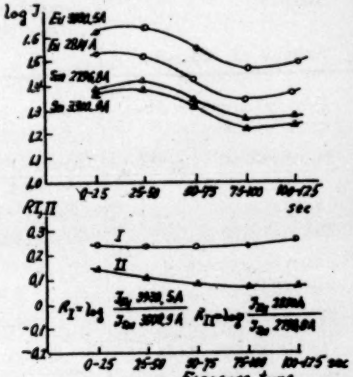

Fig. 5. Relation between the absolute and relative line intensities of samarium and europium, and exposure time.

In order to demonstrate why we chose an exposure time of 60 seconds we have shown in Fig. 3 how the blackening increases with increasing exposure time, and not the intensities of the individual lines. For longer exposures than 60 seconds the blackening is too strong and falls within the overdevelopment range of the plate.

On the basis of these results, the pair of lines Pr II 3908 A/La II 3936.2 A was chosen as the analytical pair. We turned down the pair Pr 4223.0 A/La 4300.4 A for two reasons: first, they are located rather far apart from each other, thus complicating calculations; secondly, the Pr 4223.0 A line is weak and does not show up at low praseodymium concentrations.

For the determination of europium in samarium it was established that of the europium lines free from superposition under our conditions, it is the Eu 3930.50 A line which has the greatest intensity while the Sm II 3900.9 A is a suitable line for comparison. It was shown experimentally that in this case also the working conditions could be left unchanged (current strength 9A, interelectrode distance 3 mm); it was however more convenient to increase the exposure time in this case to 80 seconds. In view of the fact that it was especially important to get as high a sensitivity as possible for the determination of europium, the effect of an additional parameter was also studied - viz. the effect of the Sm_2O_3 to $KHSO_4$ ratio on the line intensity. On varying the ratio of Sm_2O_3 to $KHSO_4$ from 1:8 to 1:1 an interesting fact was discovered.

TABLE 2

	Praseodymium in lanthanum	Europium in samarium	
Analytical pairs	Pr 3908 A	Eu 3930.50 A	Eu 2814.0 A
	La 3936.2 A	Sm 3900.9 A	Sm 2796.8 A
Composition of sample	One part rare earth oxide + four parts $KHSO_4$	ditto	ditto
Amount of sample on electrodes	30 mg	ditto	ditto
Preliminary treatment of sample	Fusion on an electric hotplate	ditto	ditto
Electrodes	Lower electrode - copper cylinder 32 x 6 mm, opening 4.5 mm, depth 2 mm; upper electrode - copper cylinder 32 x 6 mm with a cone shaped rounded end.		
Excitation source	Sventitsky 9A arc	ditto	ditto
Interelectrode distance	3 mm	ditto	ditto
Spectrograph	ISP-22	ditto	ditto
Spectrograph slit	0.005 mm	ditto	ditto
Emulsion	Ilford Process[1]	ditto	ditto
Preliminary ignition	5 seconds	ditto	ditto
Exposure	60 seconds	80 seconds	80 seconds
Development	5 minutes at 20° in a two-solution developer[2]	ditto	ditto
Fixing	1 minute rapid action[3]	ditto	ditto
Densitometer	MF-2 microphotometer	ditto	ditto
Concentration range	from 0.3 to 10% Pr in La	0.02 to 1.0% Eu in Sm	0.1 to 10% Eu in Sm

[1] It is possible to use spectrographic plates Type 2.
[2] Solution I: 1000 ml H_2O, 9 g hydroquinone, 2 g potassium bromide, 9 g potassium bisulfite. Solution II: 1000 ml H_2O and 18 g KOH.
[3] 1000 ml H_2O, 300 g sodium hyposulfite, 60 g ammonium chloride.

In the region 1:4 to 1:3 there is a maxiumum line intensity for europium and samarium while at the same time the relative intensities of these lines are practically unchanged (Fig. 4). It was thus that the ratio of Sm_2O_3 to $KHSO_4$ which we used for further work was justified.

Since at concentrations higher than 3% the Eu line 3930.50 A was very strong it was necessary to choose for high concentrations a line which was weaker than the Eu 3930.50 A line. A suitable line proved to be Eu 2814.0 A for which the Sm 2796.8 A line was a suitable comparison line.

The relations between absolute and relative intensities of the europium lines (930.50; 2814.0 A) and of the samarium lines (3900.9; 2796.8 A) to various exposure times ranging from 0-25 seconds to 100-125 seconds are shown in Fig. 5.

The ratio of the intensities of the two pairs of lines remains practically unchanged.

The operating conditions under which we photographed the spectra for carrying out spectrochemical analysis are summarized in Table 2.

Preparation of Standards

In order to prepare standards the purest samples of the rare earths at the disposal of the chemistry laboratory were used.

The standards were prepared as follows: pure lanthanum oxide was calcined at 800-900° to constant weight. A known weight of calcined oxide was dissolved in dilute nitric acid, and the nitric acid solution transferred to a standard flask and made up to volume. In a similar way a standard solution containing a known weight of praseodymium oxide (P_2O_3) was prepared from Pr_8O_{11}. Equal volumes of lanthanum solution were taken and different amounts of Pr_2O_3 solution added to them. The precipitates formed by heating the mixed solutions with excess oxalic acid were allowed to stand overnight before filtering; the oxalates were then washed with 0.5% oxalic acid and the precipitate calcined in a platinum crucible at 900° for one hour, to form the oxides.

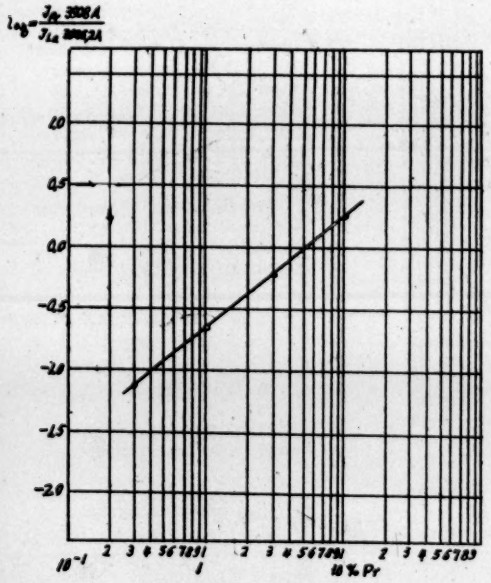

Fig. 6. Calibration curves for the determination of praseodymium.

Standards samples for the determination of europium in samarium were prepared in exactly the same way.

Two series of standards were prepared: one with 0.3, 1.0, 3.0, and 10% praseodymium in lanthanum and one of 0.01, 0.03, 0.1, 0.3, 1.0, 3.0, and 10% of europium in samarium.

Calibration Curves

The standards were photographed 4 times each under the conditions given in Table 2. The analytical lines were photometrically measured on an MF-2 microphotometer. The blackening values were converted into line intensities by means of the characteristic curves of the photographic plate. The background of the lines was taken into account in calculating line intensities. The logarithms of the relative intensities of the analytical pairs of lines were meaned for the four measurements. From these mean results calibration curves were constructed using the coordinates $\log \frac{I_{Pr}}{I_{La}}$; $\log c_{Pr}$ and $\log \frac{I_{Eu}}{I_{Sm}}$; $\log c_{Eu}$, where $c_{Pr,Eu}$ - is the concentration of europium or praseodymium in percentages.

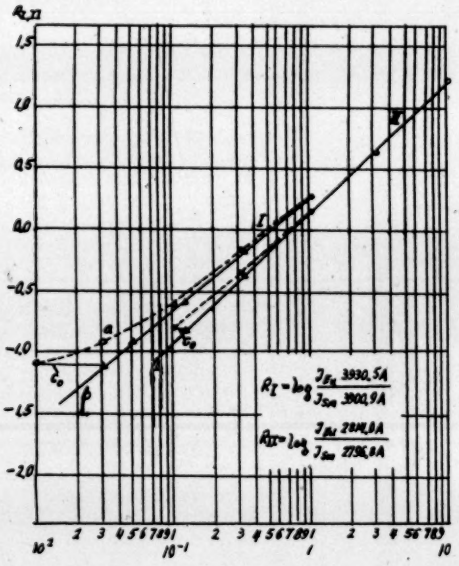

Fig. 7. Calibration curves for the determination of europium in samarium.
a - experimental curve; b - working curve.

The calibration curve for determination of praseodymium in lanthanum is shown in Fig. 6. The absence of kinks both at low and high concentrations indicate that the original materials did not contain any appreciable amounts of praseodymium, and that the line Pr 3935.82 A shows practically no interference with the La 3936.2 A line. The lower limit of determination of praseodymium in lanthanum is 0.3%.

Calibration curves for the determination of europium in samarium are shown in Fig. 7:

$$\text{I. } \log \frac{I_{Eu\ 3930.5\ A}}{I_{Sm\ 3900.9\ A}} = f(\log c_{Eu})$$

for the concentration range 0.02 to 1% and

$$\text{II. } \log \frac{I_{Eu\ 2814.0\ A}}{I_{Sm\ 2796.8\ A}} = f(\log c_{Eu})$$

for the concentration range 0.1 to 10% of europium in samarium. The experimental curves denoted by a show a slight curvature at low concentrations, which indicates that the original samarium was not completely pure, i.e. there was some europium already present. Rectification of the curve indicates that this was equal to 0.02%. The rectified working curves in Fig. 7 are denoted by b. It was confirmed by radiation analysis that the original samarium contained 0.02% Eu.

TABLE 3

Accuracy and reproducibility of the determination of praseodymium in lanthanum

Test No.	% Pr			Mean error of the mean value % Pr	Number of determinations
	Added	Average found	Difference		
3072	2.2	2.3	+0.1	±0.1	5
3073	6.5	6.3	-0.2	±0.13	5
3083	0.6	0.61	+0.01	±0.023	5
3084	1.4	1.57	+0.17	±0.045	5

Accuracy and Reproducibility.

The accuracy and reproducibility of the results for the determination of praseodymium in lathanum were studied on synthetic mixtures prepared from the pure oxides of these elements in just the same way as the standards. The results obtained are given in Table 3.

The reproducibility of the results of the determination of each unknown concentration is deduced from the mean error of the mean value of five measurements. The accuracy can be evaluated from the amount of praseodymium actually put in the test mixture and that found experimentally.

We could not use this method for preparing synthetic mixtures for the determination of europium in samarium as a means of checking the method, since the amount of europium at our disposal was limited.

TABLE 4

Checking the accuracy of the method of determining europium in samarium by comparison of spectrochemical and radiation results. Balance of absolute amts. Eu.

Number of test	Amount of Sm_2O_3, in g	% Eu found		Amount of Eu_2O_3 in mg	
		Spectrochemically	Radiation method	Spectrochemically	Radiation method
3064	61.4	0.47	0.42	250	258
3065	4.88	3.83	4.6	187	224
3066	2.25	0.59	0.48	13	11
3067	5.35	0.065	0.068	3	4
3068	0.41	0.061	0.102	-	-
3069	48.0	0.071	0.085	34	41
			$\sum_{3065}^{3069} m_{Eu_2O_3}$ =	237	280

$$m_{Eu_2O_3} = \left[\sum_{3065}^{3069} m_{Eu_2O_3}\right] \Delta - m_{Eu_2O_3}^{3064} = -13 \qquad +22$$

$$m_{Eu_2O_3} \text{ in } \% = \Delta \cdot -5.2 \qquad +8.5$$

In order to check the accuracy of the method several samples were analyzed and from these samples others were made up. These same samples were also analyzed by a radiation method in the chemistry laboratory, the activity of the Eu^{152} isotope (half-life 9.3 hours) which was prepared by irradiation of the test sample with slow neutrons being measured.

Results for the determination of the balance of the europium as determined by both methods are given in Table 4. Test 3064 was the original test material of samarium oxide from which the europium was chemically extracted. As a result an enriched[1]) sample was prepared, 3065, and a number of others containing less europium: 3066, 3067, 3068, 3069. The original amount of europium from test 3064 was distributed between tests 3065 to 3069.

From the concentrations of europium in samrium found spectrochemically and by the radiation method and from the known amounts of Sm_2O_3, the absolute amounts of Eu_2O_3 in the test samples were calculated. Ideally the total amount of Eu_2O_3 in test samples 3065 to 3069 should be equal to the original amount of Eu_2O_3 in 3064. In the last two columns of Table 4, the deviations (absolute, in mgs, and percentages) of the results of the spectrochemical and radiation methods from the ideal case are given; these deviations are -5.2% for the spectrochemical method and +8.5% for the radiation method.

TABLE 5

Reproducibility of the results of determinations of europium in samarium

Test No.	% Eu found-mean	Mean error of the mean value		Number of determinations
		in mg	in % of the value found	
3022	0.40	±0.025	±6.3	2
3038	0.665	±0.015	±2.3	2
3054	6.0	±0.025	±4.2	6
3061	0.88	±0.02	±2.3	2
3074	8.8	±0.6	±6.8	2
3075	0.97	±0.03	±3.1	2
3076	0.53	±0.01	±1.9	2
3077	0.235	0.00	0.0	2
3078	0.036	0.00	0.0	2
3079	0.035	±0.0015	±4.3	3
		Mean	±3.1	

In order to study the reproducibility of the results of the determination of europium in samarium, natural mixtures of these elements were analyzed a few times. The mean error of the mean value for each concentration indicates the reproducibility of the method (see Table 5).

SUMMARY

Despite the widely held opinion in the literature that the solution of the problem discussed above of necessity requires a spectrograph with high resolving power, we succeeded in developing a spectrochemical method for the determination of praseodymium in lanthanum (from 0.3 to 10%) and of europium in samarium (from 0.02 to 10%)by means of an ordinary spectrograph - the ISP-22 - with only average dispersion. The sensitivity of the method is somewhat lower than that of the methods employing an instrument with higher resolving power, but the difference between the results is not so great as the disparity between the means used to get the results.

[1]) Work with the object of enriching the amount of europium was carried out in the chemistry laboratory.

The spectrum is excited in an AC arc between copper electrodes. Potassium bisulfate is used as the fixing agent.

One of the rare earths originally present in the test material is used as internal standard.

A duplicate analysis requires a small amount (16mg) of rare earth oxide.

Results for the spectrochemical determination of europium in samarium have been compared with those of radiation analysis. The accuracy and reproducibility of the methods are satisfactory. It is as yet impossible to say which of the two methods - spectrochemical or radiation, is more accurate, but there is no doubt that under the conditions employed by us it is found quicker to carry out analysis by the spectrochemical than the radiation method.

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A CRYOSCOPIC METHOD FOR MOLECULAR WEIGHT DETERMINATION IN WHICH A RESISTANCE THERMOMETER IS USED

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Often, during the evaluation of the chemical properties of various industrial products, and more and more frequently in the course of scientific research, one has to resort to the determination of a very important quantity the molecular weight of the substance or the average molecular weight of a mixture). Apart from the importance of the molecular weight as such it is also essential for calculating other important constants molecular refraction, parachor, etc. Unfortunately, there is no method available which, while being rapid, is also accurate enough for molecular weight determination.

At present the most widely used method is the Beckman cryoscopic method of determining molecular weights [1], in its various modifications [2,3,4]. In order to decrease the relative error in measuring temperature differences during molecular weight determination in apparatus fitted with a Beckmann thermometer (the absolute error is of the order of 0.01°), relatively large amounts of test material are used. At high concentrations, however, the errors of determination increase because of solute association. The method of extrapolating the results of molecular weight determinations to zero concentration does not always succeed in eliminating errors arising from solute association. The author of the present article made a resistance thermometer from a semi-conductor by means of which temperature differences could be measured with an accuracy of up to 0.001° (for an accuracy of reading of 0.0005°). An apparatus was then set up and a technique worked out for the determination of molecular weights, in which the new thermometer with its advantages of accuracy and small size was utilized. In the author's laboratory an apparatus similar in construction to the one described below was successfully used for molecular weight determinations, using only 7 ml of solvent and 5-20 mg of test material.

The method described below is particularly suitable for the determination of molecular weights in large numbers since one determination does not take more than 30-40 minutes and the work is not too arduous.

The set-up used is shown in Fig. 1. The construction of the apparatus is clear from the diagram. The dimensions of the apparatus can be gauged by comparison with the scale attached to the diagram. The upper end of the control bearing 3e is welded so that the coupling rod 3d travels exactly through the opening without sticking. The lower end is welded so as to be of the same diameter as the opening, 1-1.2 mm. Such a construction for the bearing ensures that the apparatus is fairly reasonably hermetically sealed, and also ensures a smooth motion of the coupling rod without lubrication.

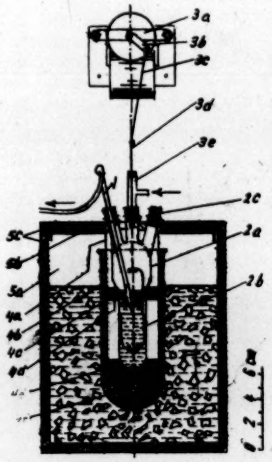
The external diameter of the stirrer 2b is 0.8 - 1 mm less than the inner diameter of the cylindrical part of the vessel 2a.

The source of dry gas (air) consisting of a 2-5 liter gas holder and a Tishchenko flask of calcium chloride, the bubble counter, and the tap for regulating the gas flow are not included in the diagram.

The bridge used for measuring the resistance of the thermometer is shown schematically in Fig. 2. Here R_o, R_o are two exactly equal wire (manganin) re-

1) Under the scientific direction of Kh. Raudsepp.

sistances wound on a common frame with parallel threads. R_0 is chosen to suit the critical resistance of the galvanometer used (from 1000 to 5000 Ω); R_x – thermometer; R_1 - a resistance box with an accuracy of not less than 0.1 - 0.2 e.g. a KMS-6; R_2 - shunt resistance (equal to ca. 0.1 of the internal resistance of the galvanometer resistance); R_3 - a resistance of 10-50 thousand Ω in series with the current supply (a flash-light battery) calculated so that the power dissipated by the thermometer as heat does not exceed 0.5×10^{-4}W; 1,2,3) switches with good (silver) contacts in the closed position; G) a null point instrument (we used an M-21 galvanometer from the USSR Ministry of Electricity factory and the experimental workshop of the Arctic Scientific Research Institute, the sensitivity of this instrument was $0.5 - 2 \cdot 10^{-9}$ A/mm and it has an internal resistance of about 500 Ω).



1-Thermometer; 2-vessel for solvent: a - vessel, b - stirrer, c - stopper; 3-stirrer drive: a- SD-60 Warren motor, b- crank (brass), c- connecting rod (wire ϕ 1 mm), d- coupling rod (stainless steel ϕ 0.5 - 0.6 mm); e- guiding sleeve (glass); 4- heat insulating flask: a- inner test tube, b- felt, c- outer test tube, d- fixing ring (cork), e- support, f- shot (lead); 5- bath: a- bath (2-3 liters), b- cover (iron), c- felt.

Fig. 1. Apparatus for the cryoscopic determination of molecular weights, incorporating a resistance thermometer.

EXPERIMENTAL

An ordinary mercury thermometer with scale divisions of 0.1° was used as a standard for calibrating the resistance thermometer. Readings were made at intervals of 2° with an accuracy of 0.01°. Calibration was carried out three times. Calibration results are superimposed on the graph of resistance against temperature. This graph then serves further for finding the temperature from the resistance measured. Small

temperature differences were calculated by means of equation (1)[1], $C_{R_{av}}$ having been calculated from the calibration results and a graph relating $C_{R_{av}}$ and R_{av} constructed beforehand:

$$\Delta t = \frac{\log R_2 - \log R_1}{C_{R_{av}}}, \qquad (1)$$

where Δt is the difference in temperature determined; R_1 and R_2 - the thermometer resistances at the two temperatures where $R_2 > R_1$; $C_{R_{av}}$ is a variable which only changes slightly with R_{av}.

As an example of the calculation of $C_{R_{av}}$ we give the following: thermometer resistance at 10.00° = 4380 Ω (log = 3.6415); at 12°C 4036 Ω (log = 3.6060); we find from equation (1) that for the average resistance 4208 Ω $C_{4208} = 0.01775$.

As an example of the calculation of the difference in temperature from differences in thermometer resistance, we instance the following: thermometer resistance at the freezing temperature of the solvent (dioxane) 4125.2 Ω (log = 3.61544); at the freezing point of the solution the resistance is 4144.9 Ω (log = 3.61751). From the graph we find that for $R_{av} \approx 4140$ Ω, $C_{4140} = 0.01764$ (R_{av} is rounded off to the nearest ten). The temperature difference is then found by means of equation (1)

$$\Delta t = \frac{3.61751 - 3.61544}{0.01764} = 0.1173°C.$$

where the fourth place of decimals is unreliable.

"Thiophene-free" grade benzene was purified by three-fold crystallization, so that half of the amount taken was finally poured off in the form of mother liquor. From this benzene 10% was distilled off as moist distillate [6], the residue being used for molecular weight determinations. "Cryoscopic" grade benzene was dried as indicated above. In both cases the freezing point of the dried benzene was 5.42-5.43°.

"Pure" grade dioxane was purified by crystallization as for benzene. The dioxane purified by crystallization was boiled for 3 hours with metallic sodium in a flask fitted with an air-cooled reflux condenser, protected from atmospheric moisture by a calcium chloride tube, and provided with a mechanical stirrer. The fraction which distilled at 101.2-101.4° was used for molecular weight determinations.

Molecular Weight Determination

Solvent (ca. 20 ml) is poured into the clean flask 2 provided for it, which has been dried at 150-170° and cooled in a desiccator (see also Fig.1) and is provided with a good cork stopper; the solvent is weighed to the nearest 0.01 g.

By slight hand pressure and using the catch, the coupling rod 3d is connected to the stirrer. A slow current of dried gas (air) is passed through the bearing. Thermometer 1 is connected after first wiping it with a dry cloth. The solvent is frozen by immersing it in ice water. Having wiped

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[1] Derived from the law for semiconductors [5].

$$\frac{1}{R} = Ce^{B/T},$$

where C and B are constants and e is the base of natural logarithms.

the outside, the vessel containing the solvent is placed in the cooling bath and the top part shielded with a strip of felt, connecting rod 3c is connected to the coupling rod 3d of the stirrer, and the motor switched on. The resistance box is adjusted to a value roughly equal to the thermometer resistance at the solvent freezing point. The current of the measuring set-up is switched on (switch 3, Fig. 2) the shunt being already on (switch 2). If during the time the solvent container is being wiped the solvent is not heated too much by the heat of the hand, then the galvanometer needle will remain within the scale limits; otherwise if the heat is too much, rapid cooling of the solvent in the ice bath should be repeated. The rate of cooling which is determined by the amount of coolant can be estimated from the displacement of the galvanometer needle. At the freezing point, the cooling rate should not exceed 1°/5-6 minutes. The solvent is supercooled about 0.4-0.6° (the extent of supercooling can be judged from the displacement of the galvanometer needle from the scale zero), the vessel containing

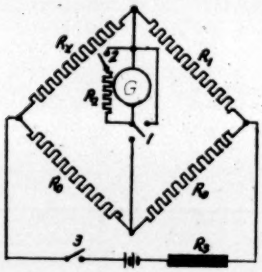

Fig. 2. Bridge used for measuring thermometer resistance.

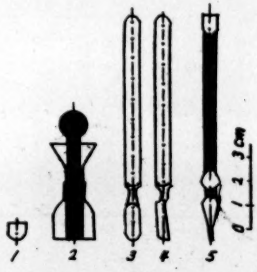

Fig. 3. Gadgets for introducing aliquots of test material.

the solvent is then lifted slightly for 5-10 seconds so that the stirrer touches the bottom. The onset of crystallization is indicated by a rapid displacement of the galvanometer needle to zero. The bridge is then balanced first with closed shunt and then with open shunt. The reading of the resistance box at the point where its resistance is equal to the resistance of the thermometer at the freezing point of the solvent is then registered. The galvanometer clamp is set (Switch 1) and the measuring set-up disconnected (Switch 3). An aliquot of the test material is then introduced into the solvent, and the thermometer resistance determined again at the freezing point of the solution, as described above.

When this technique is followed and the apparatus is in good working order, deviations in repeated determinations of the freezing points of solvent or solution do not exceed 0.0005°.

Before further use, thermometer and stirrer (3d , Fig. 1) are rinsed with pure solvent and dried.

The method used for adding the test material to the solvent depends on the state of aggregation, viscosity, and volatility of the test material.

Liquids which havea low viscosity and are non-volatile, or crystalline solids, are introduced into the solvent in a weighed tube (Fig. 3, 1). Fine crystals are lightly pressed into the test tube with a gadget easily made from glass (Fig. 3, 2). Tube plus test substance are thrown through the neck (2c, Fig. 1) into the flask; it remains in the stirrer cup and liquid thrown up from the opening into the bottom of the stirrer rapidly dissolves it. Viscous substances are introduced into the solvent by means of a boat (Fig. 3, 3,4) which is held horizontally during weighing. The boat is fixed to the neck 2c (Fig. 1) with a stopper. (The aliquot is dissolved by warming the solvent with the hand and shaking. The boat is then removed and the neck 2c (Fig. 1) closed with a stopper.

Aliquots of volatile materials are measured out in a clean weighing pipet (Fig. 3, 5) in such a way that the upper bulb remains dry. The lower capillary is "sealed" by touching it to a layer of relatively high-molecular-weight, dry, viscous oil (e.g., a lube oil or castor oil) spread out on glass, the pipet is carefully wiped and weighed. 0.01-0.02 mg of a high molecular weight material used as a seal cannot lead to appreciable errors in the determination of the molecular weight of a volatile and consequently low-molecular-weight compound (10-30 mg). The pipet containing the test is immersed in the solvent and its contents blown out. Solvent is sucked up into the pipet once or twice to rinse out any test material remaining in it. The solvent rinses are blown out each time.

Different values are given for the various cryoscopic constants in different text-books (e.g., for benzene, values from 5.00 to 5.14); these values are best determined experimentally. We determined these constants for benzene ($K = 5.10 \pm 0.02$) and dioxane ($K = 4.64 \pm 0.02$). The solvents used were pure, dry naphthalene and phenyl salicylate.

TABLE 1
The molecular weights of some substances determined in moist and dry cryoscopic benzene respectively

Designation of sample	Concentration (in %)	Molecular weight found		Molecular weight calculated
		Dry benzene $t_{freeze} = 5.42°C$	Moist benzene $t_{freeze} = 5.38°C$	
Thymol.....	0.3	149.8	148.8	150.2
	0.6	149.3	150.8	
	1.2	151.1	154.0	
Naphthalene.....	0.3	127.9	127.7	128.2
	0.6	127.8	128.3	
	1.2	128.6	129.5	
2-Naphthol	0.3	143.8	147.5	144.2
	0.6	144.6	148.1	
	1.2	146.2	155.3	
Fraction of bituminous resin boiling at 250-275° under a pressure of 10 mm Hg.....	0.3	312	304	
	0.6	314	314	
	1.2	316	324	
	1.2	-	331[1]	
	2.4	-	332[1]	

[1]) Determined in benzene saturated with water at 4°; $t_{freeze} = 5.34°C$.

TABLE 2

An example of the determination of the molecular weights of several test samples in the same aliquot of solvent

First Series of Tests			Second Series of Tests		
Number of fraction	Total solvent freezing point depression in °C	Molecular weight found	Number of fraction	Total solvent freezing point depression in °C	Molecular weight found
51	0.0815	157	89	0.1030	147
63	0.1775	157	63	0.2030	152
72	0.2800	150	72	0.2705	147
79	0.3695	155	63	0.3650	159
89	0.4595	144	51	0.4785	160

TABLE 3

Examples of the determination of molecular weights by the method described

Test material	Solvent	Concentration in %	Molecular wt. found	Concentration in %	Molecular wt. found	Molecular wt. calculated
Salol	benzene	0.5	214.2	1.0	214.6	214.2
Salol	dioxane	0.5	214.0	1.0	214.4	214.2
Naphthalene	benzene	0.3	127.9	0.6	127.8	128.2
Naphthalene	dioxane	0.3	128.0	0.6	128.4	128.2
2-Naphthol	benzene	0.3	143.8	1.2	146.2	144.2
Thymol	benzene	0.3	149.8	1.2	151.1	150.2
Thymol	dioxane	0.3	149.9	0.6	150.4	150.2
Dioxane	benzene	0.2	89.7	0.4	89.6	88.10
Benzene	dioxane	0.2	79.6	0.4	79.7	78.1
Stearic acid	benzene	0.1	289	0.2	360	284.5
Stearic acid	dioxane	-	-	0.7	284	284.5
Oleic acid	dioxane	-	-	0.8	285	282.5
Benzoic acid	dioxane	0.15	123.6	0.8	123.4	122.1
Salicyclic acid	dioxane	0.4	139.3	0.8	140.0	138.1
Pyrocatechol	dioxane	0.2	111.8	0.8	111.5	110.1
Resorcinol	dioxane	0.35	111.3	0.8	111.7	110.1
Hydroquinone	dioxane	0.3	110.9	0.7	111.2	110.1
Methylhydroquinone	dioxane	0.4	125.0	0.75	125.3	124.1
Benzanilide	dioxane	0.2	197.5	-	-	197.2
Cholesterol	benzene	0.5	378	1.1	378	386.4
Shale oil	benzene	0.6	1525	0.9	1495	-

Molecular weights were calculated by means of a formula which takes into account the freezing out of part of the solvent as a result of supercooling

$$M = \frac{K \cdot G \cdot 1000}{L \cdot \Delta t(1 - atscs.)},$$

where M is the molecular weight; K is the cryoscopic constant; G is the weight of solute in g ; L is the weight of solvent in g; Δt is the depression of the freezing point in °C or °T; a is a constant which depends on the thermal capacity and heat of fusion of the solvent and on the mass and thermal

capacity of those parts of the apparatus which come into contact with the solvent; t_{scs} - supercooling of solvent in °C.

In our apparatus the value of a was 0.014 for benzene, 0.012 for dioxane and 0.043 for nitrobenzene (calculated from the results given in [7]).

Discussion of Results

It was established that during these cryoscopic determinations when the stirring was inadequate, foam-like crystallization of the solvent on the vessel walls could be observed, which affected heat exchange, and as a consequence the freezing point temperature of the solvent or solution could not be accurately determined. The stirrer we used, however, guaranteed intensive stirring.

It is important that during these cryoscopic determinations the cooling bath should remain steady. The easiest way of ensuring this is to work with an ice bath. In order to attain a slow cooling rate, we used thermal insulation which was stronger than usual (Fig. 1, 4).

It has been pointed out in the literature [2,3] that measures to eliminate the effect of atmospheric water vapor are essential when using hygroscopic solvents. It is also known, however, that all solvents which are reasonably dry are very hygroscopic. E.g., during successive freezings of benzene in the molecular weight apparatus used under normal conditions, the following decreasing values of the freezing temperature were obtained: 5.4205, 5.4170, 5.4130, and 5.4100°C, which indicate absorption of atmospheric water by benzene. As a rule, when working in a dry atmosphere the solvent freezing temperature remains a constant with time.

The effect of moisture in benzene on the results of molecular weight determinations was therefore studied. The results are given in Table 1.

The results given in Table 1 show that other conditions being equal, association is greater in moist solvent than in the dry solvent. It is also clear that determination of molecular weights in benzene saturated with water at 4° [2] leads to high values.

The use of pure and dry solvents and small aliquots of test material enables one, in certain cases, to use one aliquot of solvent for the determination of the molecular weights of several substances when the technique described above is used. An example is given in Table 2 of the determination of the molecular weights of five chromatographic fractions isolated from bituminous resin; only one aliquot of benzene is used. In the second series of tests the aliquots of test material are added in the reverse order to that of the first. The good agreement between the results of the parallel series of experiments within the limits of accuracy of the method indicates the absence of errors as the result of association. The use of only one lot of solvent for several determinations is advantageous primarily because of the time saved. When this method is used for polar compounds (phenols) greater deviations were obtained between parallel test series.

Table 3 contains results of molecular weight determinations on a number of pure compounds in benzene and dioxane.

From Table 3 it is clear that there is no need to extrapolate the molecular weights found at concentrations of solute less than 1 to zero concentration in the solution. This fact simplifies the work considerably. It is evident from Table 3 that dioxane is a good solvent for the determination of the molecular weights of dihydroxy phenols and carboxylic acids.

SUMMARY

1. A new cryoscopic method of determining molecular weights has been worked out which involves the use of a resistance thermometer.

2. It has been confirmed that an important condition for getting reproducible results when using a cryoscopic method is to maintain heat exchange constant during the experiment; this is attained by careful heat insulation, efficient and uniform stirring, and the use of a constant temperature bath. An apparatus has been constructed which satisfies these requirements.

3. It has been confirmed that it is essential to carry out molecular weight determinations in a dry atmosphere and in a dry solvent.

4. It has been shown that there is no need to extrapolate results to zero concentration of solute in solvent if the concentration employed is low.

5. It has been shown that if low concentrations of solute are used, benzene can be used as a solvent for the determination of molecular weights of mono-hydroxy phenols.

6. It has been shown that dioxane is a good solvent for the determination of the molecular weights of dihydroxy phenols and carboxylic acids.

7. New methods have been worked out for introducing aliquots of test material into the solvent during cryoscopic determinations, which eliminate loss of solvent and are characterized by their simplicity.

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HIGH-FREQUENCY TITRATION. I

V.A. Zarinsky and D.I. Koshkin

Principle of the Method and the Apparatus Used

In recent years a number of review articles and papers devoted to experimental work have been published on the application of radio frequency currents (from 10,000 cycles to hundreds of megacycles) to volumetric analysis and for physico-chemical research [1-30].

In this method the test solution is placed in a thin walled glass cell (beaker, test tube, tube) on the outer wall of which is wound either two metallic strips insulated from one another, or a wire spiral (Fig. 1).

A cell of this type which acts in the first place as a condenser, and in the second instance as a self-induction coil, is connected to the grid or anode circuit of a high frequency generator.

The chemical changes set up during titration affect the dielectric permeability and specific conductivity of the solution, which determine the value of the total conductivity and the capacity of the cell (see below).

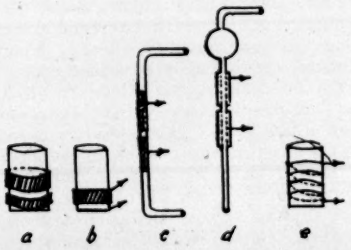

Fig. 1. Types of cells and tubes for H.F. titration and control.

a, b, c, d connected to generator as capacities, e as an induction. Tube c is used for controlling the circulating electrolyte; Tube d for sampling of test solution titrated in the beaker.

Relative changes in the electrical characteristics can be measured (according to the way the cell is connected to the generator) by changes in the value of the anode or grid current (the potential difference as well), or changes in the frequency generated, or changes in the H.F. current passing through the cell.

The equivalence point during H.F. titration in most cases is determined graphically; the relative changes of one of the quantities mentioned above are plotted along the ordiante, while the amount of reagent used (ml) is plotted along the abscissa. It is essential to note that in contrast to ordinary conductometric methods, the results of H.F. titration are not always expressed by straight lines; the curves thus obtained may have fairly complicated shapes [9 11, 25], depending on the type of H.F. generator used and on the way the cell is connected to the generator.

It is often emphasized in the literature that the accuracy of H.F. titration exceeds that of other volumetric methods [16].

It is obvious, however, that the accuracy of H.F. titration is determined in the first instance by the shape of the curves obtained in the neighborhood of the equivalence point; the accuracy will be low when the intersection at this point is not very sharp; second, the accuracy of H.F. titration depends on the same factors which are also decisive for other volumetric methods – on the rate and completeness of the reactions which proceed according to a stoichiometric equation, on the absence of side reactions between reagent and test material (or between reagent and other materials present) which could distort the position of the equivalence point. In addition, the apparatus itself has a considerable effect on the accuracy of H.F. titration. In particular, the use of the differential titration method [2] increases the accuracy even for a smooth shape for the titration curve in the neighborhood of the equivalence point. Despite a large amount of published data it is difficult to establish the practical value of H.F. titration because of conflicting claims.

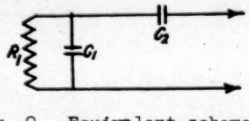

Fig. 2. Equivalent scheme for a cell with two electrodes.

Hitherto the physical processes which occur in solution during H.F. titration have not been studied; there is no doubt that these processes are more complex than those which occur during conductometric titration in which comparatively low frequencies (sonic) are used. While in conductometric titration changes in the ohmic resistance of the solution are registered, between the electrodes, during H.F. titrations the total resistance of the cell changes, and this resistance is composed of active and reactive components which depend on the generator frequency, electrolyte concentration, the area and disposition of the outer electrodes, the thickness of the glass walls of the cell [25] etc. E.g., the curve for H.F. conductivity of a given electrolyte does not change uniformly with increasing electrolyte concentration but passes through a maximum. These characteristics of H. F. conductivity curves and of H.F. titration curves can be explained by the use of electrical equivalent schemes. A cell with two metallic strips (Fig. 1 a, b, c, d) connected to a H.F. current supply can be represented by the equivalent scheme shown in Fig. 2. Here C_1 and R_1 are the capacity and resistance, respectively, of the electrolyte itself which would be observed if there was direct contact between the metallic strips and the solution; C_2 is the capacity of the metallic strips and the dielectric - glass and glass/solution boundary.

The total resistance of the cell depicted in Fig. 2 is expressed by the formula

$$z = \frac{R_1}{1 + (\omega C_1 R_1)^2} - j \left[\frac{\omega C_1 R_1^2}{1 + (\omega C_1 R_1)^2} + \frac{1}{\omega C_2} \right],$$

where the first expression is the active component, while the second represents the reactive component z; $\omega = 2\pi f$ the operating frequency of the generator; and j is an operator.

Both R_1 and C_1, which change during titration, can be experimentally determined (this requires the use of a complicated bridge set-up [9]), as well as changes in the coefficient of total conductivity (or its inverse the co-

efficient of total resistance). It is obvious that in order to use H.F. methods for analytical purposes, relations between C_2, R_1, and C_1 should be established for which changes in R_1 and C_1 would be a maximum, or show a maximal effect on changes in the total conductivity or resistance; otherwise, a H.F. set-up will not be sensitive to changes in the physico-chemical properties of a solution and a determination of the equivalence point will be impossible.[1)]

The attainment of maximal changes in R_1 and C_1 during titration is essential when they are measured separately by a bridge system or by the method of beats. In the case where the current passing through the cell is measured with a micro-ammeter we have to deal with the coefficient of total conductivity (or the coefficient of total resistance) of the cell when it is essential to realize maximal changes in the coefficient of the vector $R_1 + \gamma \cdot \frac{1}{\omega C_1}$.

Any low power tube generator can be used for H.F. titrations. If the H.F. current passing through the cell during titration is being measured, then the amplitude of the H.F. vibrations should be stabilized by using a stabilized source for feeding the generator.

If it is desired to measure changes in capacity (the cell is included in the generator circuit) then it is changes in frequency that are considered; in addition capacity changes during titration can be compensated by using a variable condenser at a fixed frequency. In this last instance it is possible to use a generator with a tuned loop in the grid and anode circuits or a quartz generator with a loop in the anode circuit.

Capacity changes in the cell connected to the anode loop rapidly change the operating conditions of the generator; this break-down in the operating conditions is registered by an indicator apparatus, e.g., a chathode voltmeter connected to the tube grid and cathode. By using a variable capacity condenser it can again be adjusted to resonate with the frequency of the otherloop or with the quartz; resonance is registered by the indicator apparatus.

The method of beats can also be used for registering changes in solution; beat frequency is measured by bringing together two oscillations which come from two generators, one of which is stabilized with respect to frequency, while the frequency of the second is determined by the loop containing the cell. This method is more complicated than the other one, since it presupposes a high degree of generator frequency stabilization, but it is more sensitive and accurate.

In order to increase the accuracy and sensitivity of the H.F. titration of solutions containing high concentrations of other electrolytes, the use of a generator operated at a frequency of up to one hundred megacycles has been recommended [29]. This condition is determined by the empirical relation

---

1) The electrical behavior of a cell can also be described by means of the total conductivity $\underline{y}$ which is the inverse of total resistance [25].

$$y = \frac{1/R_1\omega^2C_2^2}{1/R_1^2 + \omega^2(C_1 + C_2)^2} + j\,\frac{\omega C_1/R_1 + \omega^3C_2C_1^2 + \omega^3C_2C_2^2}{1/R_1 + \omega^2(C_1 + C_2)^3}$$

(the legends are the same as above).

λc = const, where λ is the radio wave length corresponding to maximal absorption of energy by a solution of the given electrolyte, while c is the concentration [30] according to published data; a set-up (operating on the beats method) with frequencies up to ca. 300 megacycles enables one to analyze solutions with a total molar concentration of electrolytes in them of up to 1 M/liter.

EXPERIMENTAL

Set-up using a 4-megacycle generator

In the set-up which we developed for H.F. titration, a H.F. voltage (4 megacycles) from a generator (Fig. 3) is fed through a variable condenser of low capacity, which serves to regulate this voltage, to one of the strips 3) on the glass tube 1) (Fig. 4). A detector 4) and an H.F. choke coil 5) are connected to the second strip on this tube; this choke is used to complete the circuit of the detector-galvanometer with respect to direct current.

The voltage rectified by the detector is passed on to the indicator-microammeter; in order to make the readings of small current changes more accurate the initial deviation of the micro-ammeter needle is compensated from the source of direct current (compensating element C.E.) (Fig. 3). The generator was set up as follows: tuned grid – tuned anode with a quartz crystal in the grid of tube 6PZ with parallel supply. The anode voltage was stabilized with stabilivolts SG-3 and SG-2. A comparatively powerful tube was chosen so

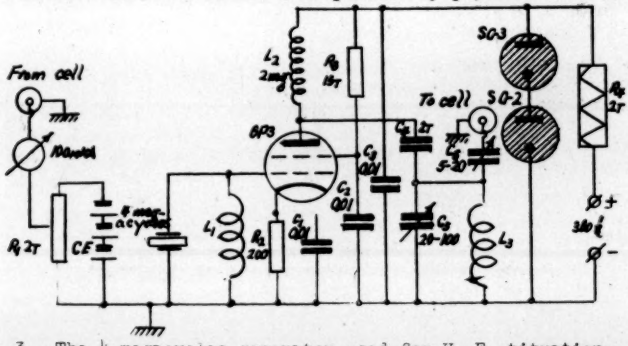

Fig. 3. The 4 megacycles generator used for H. F. titration.

that the amplitude of vibration of the HF generator changed as little as possible with changes of the load on the anode circuit of the generator during titration.

The H.F. voltage from the generator to the cell is passed through a coaxial cable; the voltage from the detector 4 arranged inside the sheathing 2, (Fig. 4) to the microammeter fixed on the front panel of the generator is also passed through a coaxial cable. The use of a coaxial cable for connecting detector to microammeter is essential in order to eliminate all possible interferences. A simple screened cable could also be used for this purpose.

The components are arranged on the front panel (Fig. 5) as follows: the tuning knob of the variable condenser of the anode circuit, 1; the knob of the variable condenser of the coupling between generator and cell (attenuator), 2,; knob of the potentiometer used for compensating for the initial

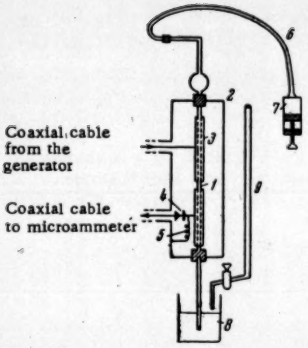

Fig. 4. Cell set-up for titration:

1) Tube for sucking up solution during current measurement; 2) tin screen· 3) a strip of aluminum foil; 4) detector; 5) induction coil; 6) rubber tube; 7) medicinal syringe; 8) beaker for titration solution; 9) buret.

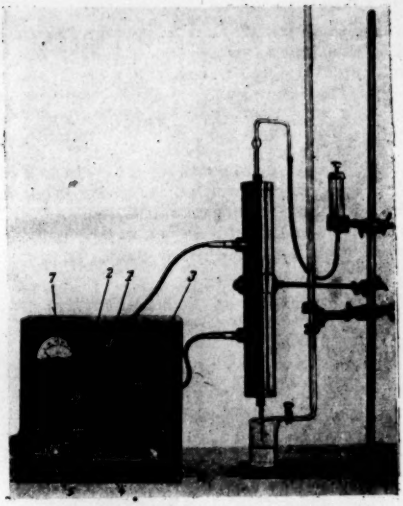

Fig. 5. General view of the set-up used for H.F. titration with a 4-megacycles generator.

deflection of the galvanometer 3, circuit switch 4, and the coaxial outlet and inlet sockets for H.F. voltage and microammeter, 5, and 6, respectively.

The titration curves obtained with this instrument are drawn from the microammeter readings which indicate the value of the H.F. current passing through the solution.

The solution to be titrated is poured into the beaker, 8 (Fig. 4), and is drawn into tube 1, for measurement of the initial current with the microammeter. After pouring the solution from tube 1 back again into beaker 8, a definite volume of reagent is added from buret 9; the contents of beaker 8 are transferred again into tube 1 for measuring the current, etc.

Results and discussion of results

Results of titration of 0.1, 0.01, and 0.001 N solutions of HCl with KOH solutions (0.446, 0.046, and 0.0046 N, respectively) are shown graphically in Figs. 6, 7, and 8.

In each case 5 ml of the HCl of the respective concentration was placed in beaker 8 for titration: for this amount of HCl the amounts of KOH should be 1.12, 1.08, and 1.08 ml for the various KOH strengths.

From the shape of the curves in Figs. 6, 7, and 8, one can conclude that during the neutralization of a strong acid (HCl) with a strong base (KOH) there is a decreasing concentration of H^+ which determines the increase in total cell resistance, and thereby the fall in current up to the equivalence point – after which the current increases again as the total resistance falls on the appearance of excess mobile OH ions.

Fig. 9 represents the titration of 10 ml of a solution of Mohr's salt (0.0086 N with respect to Fe^{II}, 0.1 N with respect to H_2SO_4) with 0.1 N $KMnO_4$; in the given instance the equivalence point determined experimentally (0.85 ml of 0.1 N $KMnO_4$), practically coincides with the calculated value (0.86 ml).

The shape of the curves during oxidation of $Fe^{II} \longrightarrow Fe^{III}$ (Fig. 9) by MnO_4^- ions can also be explained by the disappearance from solution of mobile H^+ ions bound as H_2O according to the reaction:

$$MnO_4^{2-} + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+} .$$

Fig. 10 represents the titration of 10 ml of 0.01 N $Na_2S_2O_3$ (containing 0.02 g KI as another electrolyte) with 0.1 N iodine; the equivalence point determined experimentally (0.95 ml 0.1 N I_2), differs somewhat from the calculated value (1 ml of 0.1 N I_2), probably because the intersection of the curves at the equivalence point is not clear cut enough.

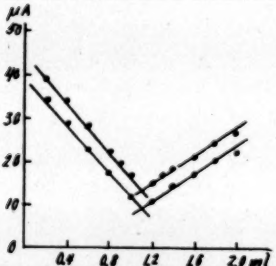

Fig. 6. Titration of 5 ml 0.1 N HCl with 0.446 N KOH. Equivalence point 1.1 ml; stoichiometric equivalence point 1.12 ml.

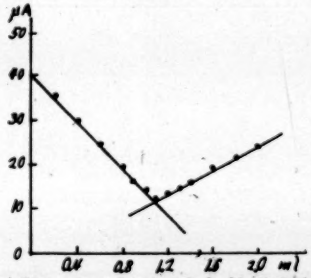

Fig. 7. 5 ml of 0.01 N HCl titrated with 0.046 N KOH. Equivalence point 1.08 ml; stoichiometric equivalence point 1.08 ml.

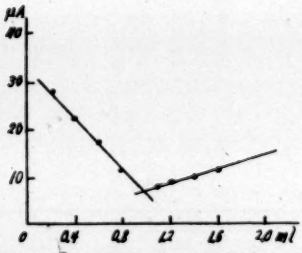

Fig. 8. Titration of 5 ml 0.001 N HCl with 0.0046 N KOH. Equivalence point 0.98 ml; stoichiometric equivalence point 1.08 ml.

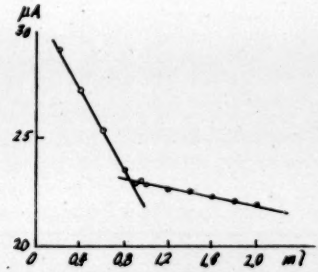

Fig. 9. 10 ml of Mohr solution (0.0086 N with respect to Fe^{II}, 0.1 N with respect to H_2SO_4) titrated with 0.1 N $KMnO_4$. Equivalence point 0.85 ml of 0.1 N $KMnO_4$; stoichiometric equivalence point 0.86 ml.

During titration of thiosulfate with iodine the increase in current up to the equivalence point is determined by the increasing concentration of mobile I^- ions which are formed during the reaction. After the equivalence point the current increases slowly, as a result of increasing KI concentration present in the titrated solution of iodine.

Fig. 11 represents the titration of SO_4^{2-} ions with $BaCl_2$. 10 ml of 0.01 N H_2SO_4 was titrated with NaOH using Methyl Red as an indicator; titration with 0.1 N $BaCl_2$ was carried out after addition to the solution of 4 ml ethyl alcohol (in order to lower the solubility) and a few milligrams of crystalline barium sulfate (to act as centers of crystallization for the $BaSO_4$ formed during titration).

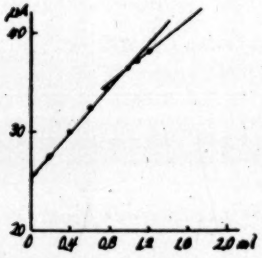

Fig. 10. Titration of 10 ml 0.01 N $Na_2S_2O_3$ (containing 0.02 g KI) with 0.1 N I_2. Equivalence point 0.95 ml, stoichiometric equivalence point 1 ml of 0.1 N I_2.

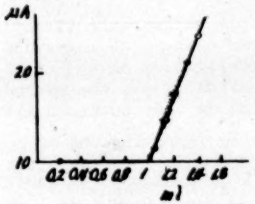

Fig. 11. Titration of 10 ml 0.01 N Na_2SO_4 (in the presence of alcohol and crystals of $BaSO_4$) with 0.1 N $BaCl_2$. Equivalence point 0.99 ml; stoichiometric equivalence point 1 ml.

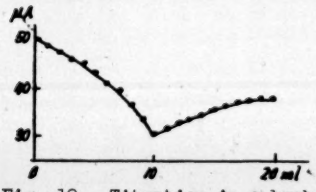

Fig. 12. Titration in a beaker-cell. Generator, 40-megacycle. 10 ml of 0.1 N H_2SO_4 titrated with 0.1 N NaOH. Equivalence point 10 ml.

The equivalence point is determined by the sharp break in the titration curve at 0.99 ml of 0.1 N $BaCl_2$ with an experimental error of ca. 1%. As shown in Fig. 11, the current remains a constant to the equivalence point; it remains constant because the total electrical conductivity is constant. The sulfate ions which are linked with Ba_2^+ are replaced in solution by Cl ions. The sharp increase in electrical conductivity at the equivalence point corresponds to the appearance of excess $BaCl_2$ in solution

On the basis of the shapes of all the curves shown above, we can conclude that the electrical behavior of a solution during H.F. titration when a method involving measurement of current is used, is analogous to its behavior in ordinary conductometric titration [26]. In other words, the change in total resistance of the cell containing a solution, as expressed by formula (1), is in this method determined basically by the resistance of the solution ΔR_1 and not by capacity changes ΔC_1 during titration.

The examples adduced here as well as other work carried out by us on volumetric analysis (precipitation reactions, oxidation - reduction) indicate that the set-up which we have developed can be used for analytical purposes. However the necessity of transferring the titration solution from the beaker into the tube for measurement of the H.F. current (Fig. 4) led us to develop a second variant of the set-up so that titration of the solution and measurement of the H.F. current could be carried out in the same beaker (beaker 4).

On attempting to titrate solutions in the cell-beaker with glass walls 0.08 cm and a diameter of 2.18 cm fitted with two external metallic strips 1.5 cm wide, and using the set-up described above with a 4 megacycle H.F. generator, we were unable to get any appreciable changes in the original value of the current as read on the microammeter.

We found however, that on using a 40 megacycle H.F. generator the changes in the current passing through a solution contained in the cell-beaker described above were appreciable, and the equivalence point of various reactions could be determined fairly accurately.

Fig. 12 depicts the titration of 0.1 N H_2SO_4 with 0.1 N NaOH in the cell-beaker using a 40 megacycle generator. The equivalence point determined by the intersection of the right and left branches of the curve coincide with the calculated value; the reproducibility of the titration curve is, however, not so good as that obtained with a 4 megacycle set-up.

Work on improving the 40 megacycle generator (stabilizing the readings of the microammeter during titration) continues.

SUMMARY

1. A set-up has been worked out for H.F. titration in which a 4 megacycle generator is used in conjunction with a quartz crystal. Using acid-alkali, oxidation - reductions, and precipitation reactions as examples, it has been shown that this set-up can be used for volumetric analysis.

2. The nature of the titration curves in all the cases examined indicates that the change in total resistance of cell-solution during titration by the method of current measurement is determined basically by changes in solution resistance.

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THE QUANTITATIVE DETERMINATION OF SULFUR IN ORGANIC MATERIALS AND FUELS USING CHROMIC OXIDE AS A CATALYST

P.N. Fedoseev and R.M. Lagoshnaya

There are already many methods in the literature for the quantitative determination of sulfur in organic materials and fuels, but still more appear all the time. On the one hand, this fact shows that there must be drawbacks to the existing methods of sulfur determination, while on the other hand it also demonstrates the importance and practical significance of this analysis in relation to the complexity of problems which contemporary organic chemistry has to solve.

The most widely used method for the determination of sulfur in organic compounds is the Carius method, which has been known for a long time.

Eshk's method is the standard method for the determination of total sulfur in fuels. The drawbacks of both methods are well known. Analysis by these methods takes up a lot of time and requires a lot of experience. Determination of combustible sulfur in fuels is carried out at present in a combustion tube using a stream of air or oxygen [1,2,3,4].

The determination of sulfur in organic compounds by combustion in a stream of oxygen has not hitherto been widely accepted, despite the simplicity of the method and the ease with which it can be carried out.

The reasons for this state of affairs are, in our opinion, as follows:

1. Complications which arise during the combustion of organic materials, particularly highly volatile ones, in a current of oxygen (spluttering, fierce combustion). This often leads to incomplete combustion of the test sample, with its consequent effect on the accuracy of the method.

2. The poor absorbability of the vapor of sulfur trioxide by the absorbent leads to losses which are also reflected in loss of accuracy. In this connection, investigations have been carried out by various workers to remove these drawbacks and to improve the method [5]. These drawbacks, however, have not been completely eliminated .

In our current work we have tried to improve, simplify, and make sulfur determinations more reliable and complete. We partly succeeded in doing this by using amorphous chromic oxide, which is readily available, as a catalyst, and at the same time trapped the reaction products in a closed, evacuated flask.

Amorphous chromic oxide is one of the most active catalysts for a number of oxidation reactions [6], particularly for the oxidation of SO_2 to SO_3 [7]. The good oxidizing capacity of this catalyst has been confirmed during quantitative determination of carbon and hydrogen [8,9].

As our work has shown, when excess oxygen is used in the presence of chromic oxide, there is practically 100% formation of sulfur trioxide. The use of a surface-burning catalyst such as chromic oxide allows the combustion rate of test material to be regulated, since combustion proceeds on

the catalyst surface without spluttering or without ignition of the sample. Highly volatile liquids can therefore be easily determined. Analysis is carried out in a high melting glass or transparent quartz tube 16-20 mm in diameter and 550-750 mm long. Combustion is carried out in an empty tube; the catalyst is only spread on the sample in a porcelain boat. Combustion products are collected in a vessel which has been evacuated beforehand and which contains a solution of alkali hydroxide or sodium carbonate with 3% H_2O_2.

EXPERIMENTAL

The apparatus used for sulfur determination by the method outlined above and which is illustrated in the diagram consists of a gasometer, a wash bottle containing alkali (not shown), the combustion tube a, a three way tap or clip b, a thick-walled flask c, capacity 1.5-2 liters, an electric oven d, length 350-400 mm. The chromic oxide catalyst is prepared by the thermal decomposition of ammonium bichromate

$$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + 4H_2O + N_3.$$

The bulky, light, dark-green, amorphous chromic oxide which is formed is calcined for 3-4 hours at 550-600° and then kept in a closed box. Before an analysis the combustion tube is heated in an oxygen stream at 600-700° and subsequently heated in the electric oven up to 750-850°.

25 ml of 0.1 N alkali or soda is introduced into the flask c followed by 2-3 ml of 3% H_2O_2; the flask is then evacuated to 10-15 mm residual pressure.

Flask c is connected to tube a, from which the air has been expelled with oxygen, tap b is carefully opened, and a slow stream of oxygen allowed to pass.

The test material is placed in boat e which has been heated beforehand in the oxygen stream. The amount of test material should be 0.1-0.2 g for organic materials, but for fuels this may be increased to 0.6-0.8 g. Larger amounts are distributed between two boats. The contents of the boat are sprinkled with the chromic oxide and the whole lightly packed down. The more volatile the test material, the more chromic oxide used.

Boat e containing test sample is rapidly transferred to the combustion tube and arranged to be 1-2 cm from the electric oven.

Combustion is carried out as follows: the oven is moved onto the edge of the boat and the stream of oxygen speeded up. After ignition the oven is moved back to its original position. The combustion process is followed by means of the incandescence of the catalyst surface. The oxygen is regulated so that no soot is formed. Oxygen is passed through at the rate of 150-350 ml/minute, according to the nature of the test material.

The more volatile the test material the more oxygen is required and the more carefully must the analysis be controlled. To ensure complete combustion we recommend an electric oven which is 400-450 mm long, particularly for strongly burning materials. In our work we used a 250-320 mm long oven and got satisfactory results for the materials tested.

TABLE 1

Expt. No.	Designation of compound and its formula	% Sulfur		Difference
		Found	Calculated	
	Volumetric method			
1	Sulfosalicylic acid	12.46	12.61	-0.15
		12.45	12.61	-0.16
2	Bis- (1,1-dimethyl-4-pentene-3-one)--sulfide	12.50	12.61	-0.11
		12.60	12.61	-0.01
	Gravimetric method			
3	Naphthionic acid	13.96	13.81	+0.15
		14.10	13.81	+0.29
4	Diphenylthiourea	13.80	14.04	-0.24
		13.88	14.04	-0.16
5	n-Toluenesulfamide	18.55	18.71	-0.16
		18.74	18.71	+0.03
6	Anhydrous sulfanilic acid	18.29	18.51	-0.22
		18.35	18.51	-0.16
7	Thiosemicarbazide	34.96	35.17	-0.21
		34.95	35.17	-0.22
8	p-Aminobenzosulfamide	18.78	18.64	+0.14
		18.80	18.64	+0.16
9	2-p-Aminobenzosulfamidopyridine	12.88	12.86	+0.02
		13.05	12.86	+0.19
10	4-Sulfanilylsulfanilamide	19.40	19.59	-0.19
		19.56	19.59	-0.03
11	2-p-Aminobenzosulfamidothiazole	24.81	25.11	-0.30
		24.90	25.11	-0.21
12	Phthalylsulfathiazole	15.77	15.89	-0.12
		15.71	15.89	-0.18
13	2-Sulfanilamido-4,6-dimethylpyrimidine	11.59	11.52	+0.07
		11.29	11.52	-0.23

Combustion takes 2-3 minutes. When larger amounts of material are tested the time taken is longer, 5-6 minutes.

When combustion is complete the boat is heated for a further 3-4 minutes, using a slow oxygen stream. The combustion products, including the mist-like sulfur trioxide, enter the evacuated flask. For a high throughput of oxygen during combustion, considerably more mist-like sulfur trioxide is formed.

TABLE 2

Expt. No.	Designation of coal sample	% Combustible sulfur[1]		Difference
		Found	Calculated	
	Volumetric finish			
1	Coal W^a = 0.99; A^c = 22.93	3.02	2.93	+0.09
		3.08	2.93	+0.15
2	Coal W^a = 8.00; A^c = 34.03	3.44	3.48	-0.04
		3.30	3.48	-0.18
3	Coal W^a = 5.86; A^c = 18.82	2.18	2.23	-0.05
		2.27	2.23	+0.04
4	Coal W^a = 2.83; A^c = 17.25	1.89	1.93	-0.04
		2.10	1.93	+0.17
5	Coal W^a = 0.59; A^c = 6.90	1.00	0.98	+0.02
		1.02	0.98	+0.04
6	Angrensky coal W^a = 9.29	2.63	2.70	-0.07
	A^c = 17.42			
	V^g = 34.25	2.60	2.70	-0.10
7	Komorovsk coal W^a = 6.24	4.93	4.88	+0.05
	A^c = 33.76	4.92	4.88	+0.04
	V^g = 36.71			
8	Bulgarian coal W^a = 10.65	4.52	4.56	-0.04
	A^c = 16.99			
	V^g = 56.64	4.77	4.56	+0.21
9	Coal W^a = 9.29; V^g = 34.25	2.53	2.70	-0.17
		2.72	2.70	+0.02
	Gravimetric finish			
10	Coal W^a = 0.96; A^c = 17.05	5.27	5.14	+0.13
	V^g = 19.45	5.29	5.14	+0.15
11	Anthracite W^a = 1.62; A^c = 22.31	4.76	4.86	-0.10
	V^g = 7.9	4.80	4.86	-0.06

[1]) Combustible sulfur was calculated from the difference between sulfur determined by the Eshk method and sulfate sulfur.

After the oven has been switched off and the pressure in the apparatus is low, it is allowed to stand for 30-50 minutes to allow for complete precipitation of the sulfur trioxide and the contents of the flask to clarify completely. The apparatus is then dismantled, the boat is withdrawn from the tube, the inner parts of tube apparatus are washed out a few times with distilled water. These washes are combined with the main volume in the absorption flask (flask c). SO_4^{2-} is determined gravimetrically or volumetrically, depending on the nature of the test material. E.g., when sulfur is determined in compounds which also contain nitrogen and halogens, nitric acid and the hydrogen halides formed interfere with volumetric determinations. Under such conditions sulfur is determined gravimetrically.

It is convenient to carry out any titrations directly in the receiver. For gravimetric determinations the contents are transferred to a beaker and the receiver washed out a few times with distilled water. The total volume of titrant should be ca. 150 ml. SO_4 is precipitated with barium chloride. An analysis involving a volumetric finish takes 50-60 minutes.

Table 1 contains results of determinations of sulfur in pure organic compounds which illustrate the accuracy of the method.

The applicability of this method for the determination of combustible sulfur was also checked.

Results of various coal analyses are given in Table 2.

SUMMARY

1. A method has been worked out for the quantitative determination of sulfur in organic compounds and fuels (combustible sulfur).

2. The method discussed differs from those described in the literature in that the gaseous reaction products are collected in a closed and previously evacuated receiver, which excludes loss as a result of carry over of mist-like sulfur trioxide.

3. The accuracy of the method lies within the limits of 0.1-0.3%.

4. A combustion followed by a volumetric finish does not take more than one hour .

5. The technique employed and the apparatus itself are simple and reliable.

6. Materials containing either high or low amounts of sulfur can be analyzed by this method.

What has been said gives us grounds for hoping that this method may be widely used in laboratory practice.

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A METHOD FOR THE QUANTITATIVE DETERMINATION OF OXYGEN DISSOLVED IN ANTIBIOTIC CULTURE MEDIUM

B.P. Bruns, E.M. Savistskaya, and T.S. Petrova

Antibiotics are usually produced on an industrial scale by deep fermentation methods. Under these conditions the oxygen content of the culture medium is of particular importance for successful biosynthesis. The supply of oxygen to the system should be such that the amount of dissolved oxygen is ample for the requirement of the micro-organisms and ensures that fermentation proceeds under optimal conditions, i.e. with maximum yield of antibiotic.

Finding out the most rational method of aeration is a very important production problem. In this connection we undertook to develop a method for determining oxygen dissolved in the culture medium of the antibiotics – penicillin and streptomycin. We adopted a polarographic method for periodic oxygen determination. We used the dropping mercury electrode as cathode.

Fig. 1. Current-voltage curve for penicillin culture medium.

△ - original liquid fixed with phenol; □ - same saturated with atmospheric oxygen; ○ - same after passing nitrogen.

Heyrovsky [1], has already shown that oxygen dissolved in an electrolyte is reduced on a cathode to give a current-voltage curve consisting of two waves. The first wave develops as the result of the reduction of oxygen to hydrogen peroxide, while the second wave develops as a result of the reduction of hydrogen peroxide to water or to hydroxyl ions.

There is no need to take the complete current-voltage curve for the quantitative determination of oxygen dissolved in a liquid. It is sufficient to measure the current I at some definite voltage E chosen at a relatively horizontal part of curve I, E (Fig. 1). Under conditions where there is a linear relation between current and oxygen content at the given potential, it is possible to determine the amount of oxygen in the test solutions.

In determining oxygen in culture medium we come up against two considerable difficulties. First, both during and after taking a sample of the culture medium from the ferment, uninterrupted absorption of oxygen continues because of the respiration of the micro-organism. It is essential, therefore,

to sample in the shortest possible time and to kill the micro-organism in order to stop its respiration. The second difficulty is to overcome the fact that the test sample must not come into contact with the gaseous phase, neither during transfer to the electrolytic cell or in the cell itself, otherwise oxygen will be either absorbed or given off by the test sample.

After transfer of sample to cell the current is measured at a definite potential. A stream of air is then blown through the cell to saturate the culture medium with oxygen; the current is then measured again at the same voltage. Nitrogen is next blown through the cell to remove the oxygen completely and the current which is determined by the substances reduced at this voltage measured (Fig. 1). The values obtained for the current for a known solubility of oxygen at a given temperature allows the absolute content of oxygen in the test liquid to be determined.

EXPERIMENTAL

Sampling and Fixing Samples of the Culture Medium

Sampling from the ferment is done through a valve 1 (Fig. 2). A glass tube 3 is connected to the valve by means of a piece of rubber hose; tube 3 which is bent at right angles ends in a glass funnel 4. The liquid, passing from tube 3, leaves funnel 4 through an outlet tube 5. Initially some culture medium is passed through the funnel and a sample taken through the needle of syringe 6 fitted into the glass tube.

A glass block of known volume V is placed in the 30-ml syringe fitted with a needle of ca. 1 mm internal diameter before sampling the culture medium; ca. 1/10 of this volume of a saturated aqueous solution of phenol is then drawn into the syringe (i.e. 1/10 of 30 − V). The block is made of a lump of glass. The culture medium is sucked into the syringe to the 30 ml mark.

In order to prevent air coming into the syringe or liquid flowing out, the needle is stuck into a cork and the solution immediately mixed by means of the glass block, the syringe being inverted at least 10 times. In this way it is possible to stop respiration of the micro-organism rapidly, and to fix the content of oxygen in the culture medium.

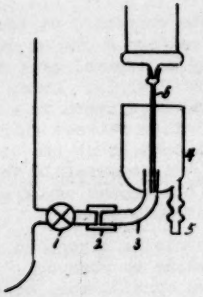

Fig. 2. Method of taking samples of culture medium from the ferment.

Construction of an Electrolytic Cell. Current was measured with a multiflex galvanometer with a sensitivity of $6 \cdot 10^{-9}$ A. A Kohlrausch bridge was used for adjusting the potential to any required value. Voltage was measured with a voltmeter calibrated to 0.01 volts. During aeration of the cell, air was supplied from a gasometer. The nitrogen, which was obtained from a cylinder, was passed over heated copper in order to remove traces of oxygen.

We found that the method suggested by Hixson and Gaden [2], of taking samples with a syringe in an atmosphere of nitrogen, gave low figures for the oxygen content because of a partial transfer of oxygen to the gaseous phase.

On letting a 0.5 M solution of sodium chloride, saturated beforehand with atmospheric oxygen, into a nitrogen atmosphere, the polarographic

current is considerably lower than the current obtained for the same solution saturated with oxygen directly in the cell itself. This method is therefore not suitable, because the amount of oxygen passing into the gaseous phase depends on the amount of it in the liquid and the method of introducing the liquid into the cell. Different values are obtained for the oxygen content, according to whether the liquid is admitted slowly along the vessel walls, or rapidly as in a jet.

We have developed an electrolytic cell the use of which ensures that the amount of oxygen in the liquid does not change during the sampling process (Fig. 3). First we passed several volumes of culture medium; section 3 was then moved into position, and the cell was thereby left full of liquid which was not in contact with a gas phase. In this way we managed to ensure that the amount of oxygen in the test material did not change either on admission into the cell or when it was in the cell itself.

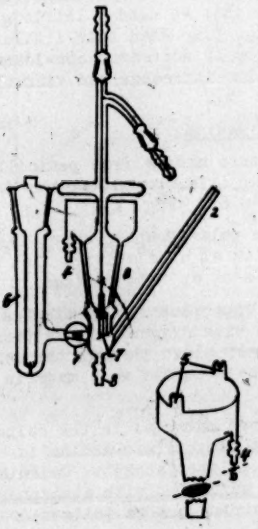

Fig. 3. Schematic diagram of the electrolytic cell used for determination of dissolved oxygen.

Liquid is admitted into the cell while the tap 1 is closed. The syringe needle is fitted into the capillary outlet tube 2, which has a flat, ground end, and the culture medium flows through this into the cell, passes along a gap in section 3 into the reservoir and leaves via outlet tube 4. During this time section 3 is raised up a little and fitted on the lugs 5. The capacity of the cell is ca. 4 ml. After about 3-4 times this volume of liquid has passed through the cell, section 3 is lowered. The culture medium which fills the cell does not come into contact with a gas phase. Contact between liquid and air in outlet tube 2 does not affect the results, since the boundary surface liquid-air is very small, while diffusion of oxygen through the liquid is extremely slow. If the liquid-air boundary has to be eliminated completely, a tap can be fitted to outlet tube 2.

A pear-shaped vessel filled with mercury is connected to outlet tube 8 by means of a rubber tube (not shown in the diagram.). While the cell is being filled with culture medium, the mercury meniscus is arranged to be at the boundary between the outlet tube 8 and the cell. While gas is being blown through, the cell section 3 is fitted onto lugs 5, and the levelling vessel of mercury lowered so that some liquid gets into tube 8. If this is not done, partial expulsion of the liquid from the cell during passage of gas is possible. Gas is led in through outlet tube 2.

In order to expel culture medium from the cell after a previous oxygen determination, section 3 is lifted a little and tap 1 is closed, while the levelling vessel plus mercury is lifted until the mercury fills all the cell. The pear-shaped levelling flask is then lowered until the mercury level is in the outlet tube 8 again. Distilled water is then passed through 2 to wash out the cell, and the distilled water itself is then ejected by lifting and lowering the mercury levelling vessel once more. This procedure is repeated

a few times. The last washings are expelled by the next lot of test culture medium.

A calomel electrode 6 is used as the anode. The use of a mercury pool anode is not suitable, since as a result of the high stabilizing properties of the culture medium the drops of mercury from the cathode do not fuse into each other, but form an emulsion of mercury-water on the mercury surface, which affects the nature of the anode.

In the opening in gap 1 a porous glass plate is fixed, and the opening on the cell side filled with agar-agar prepared in potassium chloride solution. It is possible simply to plug up the opening in tap 1 with filter paper soaked in potassium chloride.

We used a 4 cm long glass capillary with an internal diameter of 0.03-0.04 mm. The capillary was fitted into section 3. As a consequence of the low inertia of the galvanometer we observed vibrations of the galvanometer needle during measurement. In order to eliminate this we used a little glass spade 7[1], fixed at an angle to the capillary (Fig. 3). When this little spade is used, the limiting size of the mercury drop is decreased considerably, while at the same time the number of drops/unit time increases, and vibration of the galvanometer needle practically disappears [3].

Determination of Oxygen Dissolved in Culture Medium

After filling the electrolytic cell with culture medium from penicillin or streptomycin and lowering section 3 (Fig. 3), tap 1 is opened and the galvanometer deviation measured at a voltage of 0.5 or 0.6 V (Fig. 1).

For any new antibiotic to be tested, the whole polarographic curve is drawn at first. A suitable voltage is then selected at a relatively flat portion of the curve and subsequent measurements are made at this voltage.

After measuring I_x, air is blown through the apparatus for 15 minutes so that the liquid layer becomes completely saturated with oxygen. I_1 is then measured at the same voltage as I_x. Nitrogen is next blown through the solution until a constant value I_2 is obtained. All measurements were made in our case at 25 ± 0.1°C.

In view of the insignificant amount of dissolved material in the culture medium, we assumed that the solubility of oxygen in the culture medium is equal to its solubility in water, viz. $2.5 \cdot 10^{-4}$M in 1 liter at 25°. Calculation of the percentage (with respect to a solution saturated with atmospheric oxygen at 25°) and absolute content of oxygen is carried out as follows:

Percentage content

$$O2 = \frac{I_x - I_2}{I_1 - I_2} \cdot 100. \qquad (1)$$

Absolute content

$$O_2 = \frac{I_x - I_2}{I_1 - I_2} \cdot 2.5 \cdot 10^{-4} \text{ Moles/liter} \qquad (2)$$

We checked the nature of the relation between current and percentage oxygen in solution in culture media of penicillin.

Liquids with known amounts of oxygen were prepared by mixing two samples of filtered culture medium in known proportions: 1) a solution saturated with nitrogen; 2) a solution saturated with atmospheric oxygen. The liquids were

[1]) We should like to thank T.A. Kryukova for advice on the use of a mercury cathode with forced break-off of the mercury drops.

mixed in the syringe. The flasks containing the two liquids through which the gases were passed were kept in the same thermostat as the cell.

Determinations of I_x, I_1 and I_2 for liquids containing different amounts of oxygen were made first, and a curve relating current to oxygen content of the culture medium drawn (Fig. 4). Fig. 4 shows that the current is a linear function of oxygen concentration. Equations (1) and (2) can therefore be used for determination of oxygen in the culture medium.

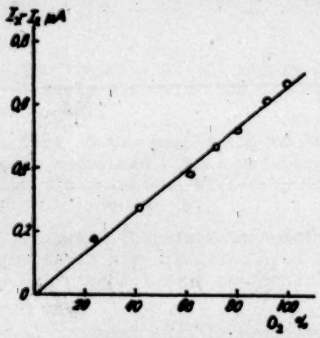

Fig. 4. Relation between the current which is a function of the oxygen reduced and the amount of dissolved oxygen in the culture medium.

The presence of micelles in the culture medium leads to an increase in variation of current strength. This is a consequence of the fact that the micelles alter the character of the convection currents developed around the mercury drops. Oxygen is usually determined in media which contain these micelles. To get more accurate results it is necessary to remove micelles by filtration or centrifuging. It follows that the conditions under which filtration or centrifuging are carried out must ensure that the culture medium does not come into contact with air.

An oxygen determination takes ca. 40 minutes.

SUMMARY

1. An electrolytic cell is described which can be used for the determination of oxygen dissolved in liquids.

2. A quantitative method has been worked out for the determination of oxygen dissolved in antibiotic culture media.

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All-Union Scientific Research Institute on Antibiotics, Moscow.

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A METHOD FOR THE QUANTITATIVE DETERMINATION OF ALKYLCHLOROSILANES IN AIR

E.A. Peregud and N P. Kozlova.

The toxicity of the vapors of silico-organic compounds poses the problem of their determination in the air of factories and industrial enterprises [1].

Very little work seems to have been done on the analysis of silico-organic compounds. What references there are in the literature refer mainly to the determination of fairly large amounts of these materials in various technical products [2,3].

In order, therefore, to determine small amounts of volatile silico-organic compounds in air, particularly vapors of alkylchlorosilanes, we carried out some experimental work on the following stages of a preliminary scheme of analysis:

1) trapping alkylchlorosilane vapors from the air;

2) mineralization of the silico-organic material and subsequent fusion of the residue;

3) a search for the optimal conditions for colorimetric determination of silica by the very sensitive silico-molybdenum blue reaction.

The method as a whole was based on this final colorimetric determination of silicon, and first of all a search had to be made for favorable conditions of carrying out the so called "blue" reaction, which would ensure stable colors and a correct proportionality between color obtained and test material. Despite the fact that getting the yellow-colored heteropoly acid, and subsequently forming the blue product by its reduction, is a widely used method for the analysis of various silicon containing compounds, there is as yet not one uniform technique of carrying it out [4].

The absence of chemical characteristics for the individual stages of the reaction and the complexity of the method as a whole may explain the abundant variety of colorimetric methods which are based on this reaction. A multitude of factors may affect the "blue" reaction, but the reducing agent used is of particular importance.

This can be explained by the fact that while the reduction reaction of the yellow colored compound $H_4[Si(Mo_3O_{10})_4]\cdot nH_2O$ is used for the determination of the central ion (Si), the color itself is determined by the reduction of the coordination ion of the complex (molybdenum). Since the complex formed is not separated from excess reagent – ammonium molybdate, then it is essential to choose reducing agents and reaction conditions such that only the molybdenum combined as the complex with silicon is reduced, and not molybdenum in excess ammonium molybdate as well [5].

Various reducing agents have been proposed for getting the blue reaction product; sodium sulfite, tin (II) chloride, benzidene acetate, metol, hydroquinone, aminonaphthosulfonic acid in the presence of sodium sulfide, bisulfite, and a number of others [6,7].

In our work, therefore, we paid special attention to choosing an easily available and suitable reducing agent, and to choosing conditions such as would ensure stable colors which are proportional to the amount of test element.

As a result of much work we chose ascorbic acid in conjunction with tartaric acid as the reducing agent of the yellow-colored complex.

In numerous experiments with known weights of silicon (Na_2SiO_3) in the form of a series of standard solutions with a wide concentration range, we obtained colors which were stable over many days and which were proportional to the amount of silicon in solution. We became convinced that tartaric acid plays an important part in the given reaction:

1) it eliminates interference from other materials which give a similar blue color (phosphate, arsenic) by destroying their heteropoly acids, and

2) tones down the strong reducing properties of ascorbic acid, ensuring selective reduction of molybdenum in the complex without touching excess molybdate.

In looking for favorable conditions for the colorimetric determination of small amounts of silicon which are described in detail in the analytical procedure farther on, we switched over to working out a method for mineralizing the silico-organic compound and converting the silicon dioxide formed into an ionic form, which could give the yellow-colored compound to be reduced to the silico-molybdenum blue.

Alcoholic solutions of methyltrichlorosilane and dimethyldichlorosilane were used as test materials. Small aliquots of test material were dissolved in ethyl alcohol, and from these solutions standard solutions of known initial concentration of the alkylchlorosilanes were then prepared.

Experimental conditions. 2 ml of the alcoholic solution of silane was introduced into a platinum crucible and 2 ml each of distilled water and concentrated sulfuric acid added. The crucible was carefully heated on a sand bath the temperature of which was gradually increased. When white vapors had ceased to come off, the crucible was calcined for a short time in a muffle, the dry residue was then carefully mixed with an anhydrous carbonate mixture (Na_2CO_3 + K_2CO_3) and fused. The fused mass was leached out with water, the solution was acidified to a weak acid reaction to litmus by addition of sulfuric acid, and then made up to standard volume with water. A known volume of solution was placed in a colorimetric tube, and the reagents added in the following order: ammonium molybdate, tartaric acid, ascorbic acid. Color intensity was then measured either by using a standard series of solutions prepared from different amounts of sodium silicate, or measured in an electric photocolorimeter (see Analytical Procedure).

TABLE 1
Results of determinations of methyltrichlorosilane

Taken, in mg	Found, in mg	Difference, %
0.872	0.931	106.7
0.654	0.665	101.7
0.437	0.434	99.3
0.327	0.308	94.1
0.218	0.213	97.7
0.175	0.172	98.3
0.087	0.087	100.0

TABLE 2
Results of determinations of dimethyldichlorosilane

Taken, in mg	Found, in mg	Difference, %
0.645	0.601	93.2
0.860	0.810	94.2
0.860	0.900	104.2
0.430	0.420	97.7
0.430	0.420	97.7
0.215	0.210	97.7
0.086	0.079	91.9

Tables 1 and 2 contain results of determinations of alkylchlorosilanes under our analytical conditions.

Having completed this stage of the investigation, the next step was to find an efficient absorbent for the complete absorption of alkylchlorosilane vapors from the air.

Of a large number of absorbents tested, the best was found to be concentrated sulfuric acid. The use of sulfuric acid as an absorbent was a very convenient one, since this acid is also used for mineralizing the test material.

TABLE 3

Absorption of alkylchlorosilane vapors by concentrated H_2SO_4

(Results expressed in mg of silicor)

No. of absorption tube	Amount found, in mg	No. of absorption tube	Amount found, in mg
1	0.564	1	0.114
2	0	2	0
1	0.435	1	0.056
2	0.012	2	0
1	0.264	1	0.043
2	0.012	2	0
1	0.240	1	0.037
2	0	2	0
1	0.125	1	0.018
2	0	2	0

Results given in Table 3 characterize the completeness of absorption of silane vapors by concentrated sulfuric acid. An essential condition for prevention of any vapor getting through is an even throughput of air, through the absorption tube, of 5 liters/hour.

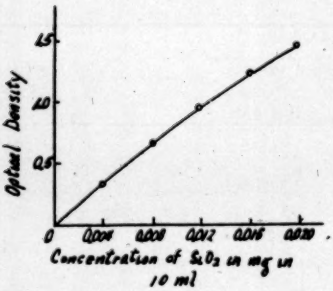
On the basis of these tests we worked out the following method for the determination of alkylchlorosilanes in air.

Analytical Procedure. Air is sampled by passing it through 2 micro-absorbers of the Polezhaev type each containing 5 ml of concentrated sulfuric acid. 5-10 liters of air, according to the expected silane concentration are drawn through the apparatus at a rate of not more than 5 liters/hour.

By regulating the throughput with a screw-clip placed between the last absorbent tube and the aspirator, surges can be avoided, and the air passes through the absorbers evenly. In order to determine momentary concentrations of vapor which arise in a short time under production conditions, air is taken into 1 liter vacuum gas pipets containing 10 ml concentrated sulfuric acid. The acid from each absorbent tube is separately quantitatively transferred to a platinum crucible (5 ml each is taken from the gas pipets), and heated on a sand bath, first carefully and then more strongly until cessation of white SO_3 fumes. 0.1 g of carbonate mixture 1:1 (Na_2CO_3 + K_2CO_3) is placed in the crucible and 3 ml of water added; the solution is mixed and evaporated to dryness, and finally calcined. The melt is leached out with 3 lots of 5 ml of hot distilled water. The solution is transferred to a flask of molybdate glass; a strip of litmus paper is introduced into the solution, which is acidified with 1 N sulfuric acid to give a very weak acid solution (the final acidity of the solution should not exceed 0.02 N), when it is heated to expel

carbon dioxide. On cooling, the solution is made up to 20 ml with distilled water in a measuring cylinder, and 4 ml taken of this solution for determination of silicon in a colorimetric tube. Blank determinations are run from time to time to check on the presence of silica in the reagents used. The last stage in the analysis is the colorimetric determination of silicon by silico-molybdenum blue formation.

In order to construct a calibration curve, various amounts from 0.1 to 1 ml of a standard solution of Na_2SiO_2 containing 0.01 mg Si/ml were introduced into a series of colorimetric tubes to cover the range 0.001 to 0 01 mg Si at intervals of 0.001 mg. The volume was made up to 4 ml in each case.



0.1 ml of ammonium molybdate solution[1]) is added to each tube, shaken and left to stand for 5 minutes for the yellow silico-molybdenum blue color to form. At the end of the five minutes, 1 ml of 5% tartaric acid and 0.1 ml 1% ascorbic acid are added to each tube with shaking. The blue color formed is measured after 30 minutes. The results obtained are calculated in terms of the number of mgs of the organosilane in 1 liter of air tested, after taking into account all the dilution factors, etc., involved.

The high stability of the colors obtained under the conditions which we have suggested for the formation of silico-molybdenum blue enables a photocolorimetric method to be worked out for silicon.

SUMMARY

1. Optimal conditions have been worked out for the determination of silicon by the formation of silico-molybdenum blue using ascorbic acid as reducing agent. It has been established that an aqueous solution of ascorbic acid in the presence of tartaric acid only reduces molybdenum combined as the complex with silicon, and does not affect excess ammonium molybdate reagent

Under our conditions the color obtained is stable with time and is proportional to the concentration of silicon in solution.

2. A method has been developed for the determination of silicon in organic compounds which is based on the mineralization of the test material with concentrated sulfuric acid, fusion of the residue with a carbonate mixture, and colorimetric determination of silicon by the "blue" reaction.

3. A method is suggested for the determination of low concentrations of alkylchlorosilane vapors in air.

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The Leningrad State Scientific Research Institute of Labor Hygiene and Occupational Hazards.

1) 18.8 g of chemically pure ammonium molybdate is introduced into a 250-ml standard flask, dissolved in water, and 80 ml of 10 N H_2SO_4 gradually added, and the solution is finally made up to the 250 mark.

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A STUDY OF THE EXTRACTION OF CHROMIUM AS PERCHROMIC ACID WITH ETHER

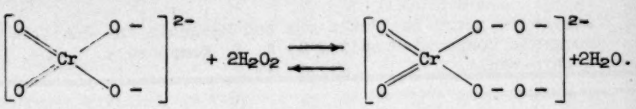
K.V. Troitsky

A study of the extraction of perchromic acid with organic solvents is of essential importance because the formation of the blue colored perchromates is one of the specific reactions for Cr^{6+} which is often used in analytical chemistry for identification of chromium.

This reaction, however, has not been studied fully enough from an anlytical point of view, since the optimal conditions for extraction using various concentrations of acids and hydrogen peroxide, have not been establ lished, nor has the effect of using different acids (HCl, HNO_3, and H_2SO_4) on the extraction process been determined.

When chromates are oxidized with hydrogen peroxide in sulfuric, nitric and hydrochloric solutions, perchromates having the composition $MeCrO_5$ and possessing a blue color are formed. It is possible to attach a molecule of hydrogen peroxide to the perchromates to form a compound $MeCrO_5 \cdot H_2O_2$ [1]. The blue potassium perchromates have the composition KH_2CrO_7, and are expressed by the formula $KCrO_8 \cdot H_2O$, since the existence of free hydrogen peroxide has not been established in these compounds [2,14].

When a solution containing potassium perchromate is shaken with ether or amyl alcohol, the solvent layer acquires a blue color [3,15]; the reaction leading to the formation of blue colored perchromic acid CrO_8^{2-} may be expressed by the following equation [4]:



Perchromic acid is more stable in ether solution than in aqueous solution.

When alkaline solutions of chromates react with hydrogen peroxide, red perchromates $MeCrO_8$ are formed, which are insoluble in ether.

A lot of work on the study of the peroxide compounds of chromium and other elements has been carried out by P. Melikov and L. Pisarzhevsky, starting back in 1897 [5,6,7]. In order to detect chromium in any solution, the following method can be used: to a small amount of a 3% solution of hydrogen peroxide is added some dilute hydrochloric acid and a few drops of ether, finally some of the slightly acidified test solution in which the chromium should be in the form of the ion $Cr_2O_7^{2-}$ is added.

If the solution contains a comparatively large amount of chromium the ether will be colored blue, while for insignificant amounts of chromium a blue ring will be formed on the boundary between ether and aqueous phases [8].

The color of the ether layer persists for several hours, if the amount of chromium in the ether layer is fairly high.

It is recommended that the reaction temperature should not be higher than 15-18°, since at high temperatures extraction of chromium and the stability of the blue color of the ether layer both decrease appreciably. Using this method chromium can be detected at a limiting concentration of 1:50,000 and in certain circumstances it is possible to detect 2.68 Cr in 5 ml solution, i.e. at a limiting concentration of 1:2,000,000 [9]. Under normal conditions this reaction is of comparatively low sensitivity, but it is characterized by high specificity, since only chromium gives a blue color with ether, and comparatively few elements interfere with the reaction.

TABLE 1[1])

Ions present	Limiting ratios	Limiting concentration for chromium	Color of interfering ions
Ag, Hg, Cu, Pb, Cd, Sb, Sn^{4+}, Au, Rh, Pd, Pt, Se, Mo, W, Nb, Ta, Al, Fe^{3+}, U, Ce Rare earths, Zr, Th, Be, Tl^{+}, Zn, Mn, Ni, Co, Ba, Sr, Ca, Na, K, Rb, Cs	100:1	1:50,000	-
Bi, Ir, Te, Fe^{2+}, Ti, Tl^{3+}	15:1	1:15,000	Fe^{2+} and Ti give yellow colors.
As	10:1	1:10,000	-
V^{3+}, V^{5+}	5:1	1:5,000	Reddish-brown color

[1]) Results given in "Reactions and Reagents for Qualitative Analysis of Inorganic Compounds" edited by A. S. Komarovsky, p 109, (1950) are used in this table.

The effect of the presence of other ions in solution on the sensitivity of the reaction for determination of chromium by extraction as perchromic acid with ether is shown in Table 1, [8]. Reducing ions affect chromium determination but on oxidation of Cr^{3+} to Cr^{6+} they are also oxidized. Ethyl acetate has also been recommended as an extracting agent. Cr^{6+} is extracted at a pH of 1.7, a concentration of H_2O_2 of 0.02 mol/liter, and at a temperature of -10°, [10].

We studied the extraction of chromium with diethyl ether from hydrochloric, nitric, and sulfuric acid solutions in order to find optimal extraction conditions. These experiments were carried out as follows: 2 ml of a solution containing a known amount of H_2O_2 and acid was introduced into a graduated test tube fitted with a ground glass stopper, a known amount of diethyl ether plus 1 ml of a K_2CrO_4 solution containing 100 γ Cr^{6+} was also added.

The solutions were shaken until the ratio of acid layer to ether layer was 3:1. If insufficient ether had been added originally, then some more was added and the shaking repeated until the required ratio of layers was obtained.

TABLE 2

Expt. No.	% Content in solution before extraction		Conc. of Cr in solution before extraction, γ Cr/ml	V_{sol}/V_{ether}	Conc. of chromium after extraction, in γ Cr/ml		Distribution coefficient	% Chromium extracted by ether	Color of layer after extraction	
	HCl	H_2O_2			ether layer	acid layer			hydrochloric	ether
1	8.0	0.0	33.3	3:1	-	-	-	0.0	yellow	colorless
2	0.0	5.1	33.3	3:1	-	-	-	0.0	reddish-brown	colorless
3	2.0	1.3	33.3	3:1	67.4	7.8	8.6	74.2	colorless	blue
4	1.0	0.63	33.3	3:1	69.7	7.1	9.8	76.6	same	same
5	0.5	0.32	33.3	3:1	73.8	3.6	20.7	88.6	same	same
6	0.25	0.16	33.3	3:1	89.2	0.58	155.0	98.1	same	same
7	0.12	0.076	33.3	3:1	71.0	4.6	15.4	85.2	same	same
8	0.06	0.038	33.3	3:1	81.7	3.1	26.5	89.8	same	same
9	0.03	0.019	33.3	3:1	69.4	7.1	9.7	76.4	pale blue	same
10	0.015	0.010	33.3	3:1	51.6	13.2	3.9	56.7	colorless	same
11	0.008	0.005	33.3	3:1	26.8	20.5	1.3	32.2	yellow	pale blue
12	0.004	0.003	33.3	3:1	-	-	-	0.0	same	colorless
13[1])	0.000	0.000	33.3	3:1	-	-	-	0.0	same	same

[1]) Extraction from aqueous medium.

Before extraction 33.3 γCr was contained in 1 ml solution. The limiting concentration was 1:30,000. Cr^{6+} was determined colorimetrically using diphenylcarbazide [11,12].

After ether extraction a sample of solution was taken from the acid layer, and treated with solid Na_2O_2 in order to convert Cr^{3+} to Cr^{6+}; the solution was evaporated to dryness on a water bath and 0.2 N HCl added to give an acid reaction; this solution was then carefully mixed for 5 minutes to remove any traces of H_2O_2, after which 1 ml of a 0.25% solution of diphenylcarbazide was added and the chromium determined colorimetrically, using a Dubosc colorimeter. The most stable violet color was obtained in hydrochloric acid solution when using diphenylcarbazide, the next most stable color was obtained in solutions of sulfuric acid and the least stable color in nitric acid solutions. When comparatively high concentrations (4-8%) of H_2O_2 were used in acid solution, a blue color was formed in the upper zone on addition of K_2CrO_4; this blue color however disappeared rapidly on shaking the solution; during this process perchromic acid breaks down and Cr^{3+} is formed, this is the result of the reducing properties of excess H_2O_2.

TABLE 3

Expt No.	% Content in solution before extraction		Conc. of Cr in solution before extraction, γ Cr/ml	V_{sol}/V_{ether}	Conc. of chromium after extraction, in γ Cr/ml		Distribution coefficient	% Chromium extracted by ether	Color of layer after extraction	
	HNO_3	H_2O_2			ether layer	acid layer			nitric acid	ether
1	8.0	0.0	33.3	3:1	-	-	-	0.0	yellow	colorless
2	0.0	5.1	33.3	3:1	-	-	-	0.0	reddish-brown	same
3	2.0	1.3	33.3	3:1	55.8	10.0	5.6	67.1	colorless	blue
4	1.0	0.63	33.3	3:1	61.2	8.0	7.6	73.5	same	same
5	0.5	0.32	33.3	3:1	64.2	8.9	7.2	70.7	same	same
6	0.25	0.16	33.3	3:1	62.1	8.0	7.8	74.5	same	same
7	0.12	0.076	33.3	3:1	60.2	8.4	7.2	72.2	same	same
8	0.06	0.038	33.3	3:1	56.6	9.7	5.8	67.9	same	same
9	0.03	0.019	33.3	3:1	47.3	13.5	3.5	56.8	same	same
10	0.015	0.010	33.3	3:1	19.3	23.9	0.8	21.2	yellow	pale blue
11	0.004	0.003	33.3	3:1	-	-	-	0.0	same	colorless
12[1])	0.000	0.000	33.3	3:1	-	-	-	0.0	same	same

[1]) Extraction from aqueous medium.

These preliminary results showed that the dry salts $K_2Cr_2O_7$ and K_2CrO_4 are not extracted by ether; this is confirmed by qualitative tests for Cr^{6+} with diphenylcarbazide.

Table 2 contains data on the effect of H_2O_2 and HCl concentrations, respectively on the extraction of perchromic acid with ether.

These results show that on changing the concentration of HCl and H_2O_2 in the interval 2-0.02% the percentage extraction of chromium by ether changes from 74 to 98. The optimal conditions for chromium extraction are observed at a content of HCl and H_2O_2 of 0.15 to 0.25%. At lower concentrations of HCl and H_2O_2 the extraction of chromium deteriorates, since under these conditions only partial formation of perchromic acid occurs. When chromic acid is extracted with ether from neutral solutions containing H_2O_2, the solution is colored a reddish-brown as a result of the formation of alkali salts of perchromic acid which are insoluble in ether [13]. Cr^{3+} and Cr^{6+} are not extracted at all with ether if neutral or weakly acid solutions which do not contain H_2O_2 are used.

Table 3 contains results for the extraction of perchromic acid from nitric acid solutions with ether.

Extraction of perchromic acid from nitric acid solutions is not so good as from hydrochloric acid solutions, the optimal chromium extraction being only 75% in the former.

Chromium extraction with ether ranges from 67-75% within a wide concentration interval (2.0-0.04%).

TABLE 4

Expt No.	% Content in solution before extraction		Conc. of Cr in solution before extraction, γ Cr/ml	V_{sol}/V_{ether}	Conc. of chromium after extraction, in γ Cr/ml		Distribution coefficient	% Chromium extracted by ether	Color of layer after extraction	
	H_2SO_4	H_2O_2			ether layer	acid layer			sulfuric acid	ether
1	8.0	0.0	33.3	3:1	-	-	-	0.0	yellow	colorless
2	0.0	5.1	33.3	3:1	-	-	-	0.0	reddish-brown	same
3	2.0	1.3	33.3	3:1	50.6	12.3	4.1	60.7	colorless	blue
4	1.0	0.63	33.3	3:1	52.3	12.9	4.05	57.5	same	same
5	0.5	0.32	33.3	3:1	59.6	10.5	5.7	65.5	same.	same
60	0.25	0.16	33.3	3:1	55.4	10.5	5.3	66.5	same	same
7	0.12	0.076	33.3	3:1	59.6	7.0	8.5	77.5	same	same
8	0.06	0.038	33.3	3:1	55.8	10.3	5.4	67.0	paleblue	same
9	0.015	0.010	33.3	3:1	21.6	23.1	0.94	26.0	pale yellow	pale blue
10	0.008	0.005	33.3	3:1	-	-	-	0.0	yellow	colorless
11[1])	0.000	0.000	33.3	3:1	-	-	-	0.0	same	same

[1]) Extraction from aqueous medium.

At very low concentrations of HNO_3 and H_2O_2, chromium extraction deteriorates, since insufficient amounts of H_2O_2 and HNO_3 are in solution to ensure formation of perchromic acid.

Table 4 contains results of extraction of perchromic acid from sulfuric acid solutions with ether.

For a content of 0.5-0.05% of H_2SO_4 and H_2O_2 in the original solution, 65-77% of chromium is extracted. Extraction of perchromic acid from H_2SO_4 solutions is inferior to extraction from either HCl or HNO_3 solutions.

The author wishes to express his thanks to Corresponding Member of the USSR Academy of Sciences I. P. Alimarin for his valuable advice.

SUMMARY

1. When micro amounts of chromium (33.3 γCr/ml) are extracted as perchromic acid with ether the best results are obtained when hydrochloric acid is used; nitric acid is inferior, while sulfuric acid is the poorest of all three.

2. The highest percentage extraction of micro-amounts of chromium with ether is attained by using comparatively low concentrations of acid and hydrogen peroxide in solution (0.1-0.5%).

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A SPOT TEST FOR COBALT

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More than 80 reactions have been put forward for the determination of cobalt. Only few of them, however, can be used as a spot test for its detection. For this purpose ammonium thiocyanate is usually used, and then only in conjunction with organic solvents and masking materials. Of the other cobalt reagents, the most suitable for spot tests are the following: potassium nitrite, ammonium tetrathiocyanomercurate, isonitrosoacetophenone, 2-nitroso-1-naphthol-4-sulfonic acid, diphenylthiocarbazone (dithizone), and dithio-oxamide (rubeanic acid).

Recently two more reagents have been added to this list: dimethylglyoxime [1], and nicotine-thiocyanate reagent [2].

According to our experiments thiourea can also be used as a spot reagent for cobalt.

Thiourea forms with cobalt salts brightly colored complexes which are soluble in water and organic solvents. The following thiourea complexes of cobalt are known: $[Co_2(CSN_2H_4)_7]Cl_4$ with a blue-black color, $[Co(CSN_2H_4)_4](NO_3)_2$ with a blue-green color, and $[Co_2(CSN_2H_4)_3](SO_4)_2$ with an intense blue color [3]. They all dissolve in alcohol, acetone, and other organic solvents to give blue colored solutions. At high concentrations their aqueous solutions are colored blue, blue-green, and green respectively, while their dilute aqueous solutions are colored a pale rose.

According to K. B. Yatsimirsky [4], thiourea gives complexes with all cations which show a tendency to form covalent bonds. It is of interest, however, that of the cations of the usual analytical groups, only two form brightly colored compounds with thiourea, viz., cobalt and bismuth. This is the basis for the use of thiourea as a spot reagent for cobalt.

EXPERIMENTAL

Detection of cobalt by means of thiourea with a known reaction sensitivity was carried out with pure solid cobalt nitrate by trituration [5], and with aqueous solutions of varying concentrations. Solid cobalt nitrate was "diluted" by mixing it with sodium nitrate.

I. Cobalt was easily detected by means of thiourea as its solid salt, as follows. A few grains of test material were triturated in a mortar with 2-3 crystals of thiourea. When cobalt is present the mixture is colored blue, blue-green, or green according to the amount of cobalt present.

Limit of identification 0.31 μg cobalt. Minimal concentration is 1:460,000.

The reaction sensitivity can be increased somewhat (the color is brightened) if the triturated mixture of test material plus thiourea is moistened with a drop of acetone.

II. Cobalt can be detected in aqueous solution by the reaction suggested, by two methods:

1) Some dry thiourea in a test tube is moistened with 1-2 drops of test solution and heated gently. If cobalt is present the mixture will be colored blue or green.

Limit of identification 1.25μg cobalt. Minimal concentration 1:40,000.

2) 1 ml of test solution is mixed in a test tube with 1 ml of a saturated aqueous solution of thiourea and the mixture heated to the boil. A strip of filter paper is then dipped in the solution, removed, and dried carefully over a hot plate or burner. If cobalt is present the paper will be colored blue, emerald green, or light green according to the cobalt concentration of the solution.

Limit of identification 2.5 μg cobalt. Minimal concentration 1:20,000.

III. The application of this reaction to the detection of cobalt in the presence of other cations was checked on a series of solutions of the following cations: NH_4^+, Li^+, K^+, Na^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Al^{3+}, Ni^{2+}, Cr^{3+}, Mn^{2+}, Ag^+, Hg^+, Hg^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Bi^{3+}, Sn^{2+}, Sb^{3+}, Ce^{3+}, Zr^{4+}, UO_2^{2+} and Th^{4+}.

The following points were established:

1) Of these cations Bi^{3+}, Cu^{2+}, Ni^{2+}, and Cr^{3+} interfere with the detection of cobalt by the use of thiourea using a trituration method.

Bismuth forms a bright yellow or orange colored complex with thiourea, which masks the blue (or green) cobalt complex color.

Ions of copper, nickel, and chromium in amounts exceeding that of cobalt in their mixtures interfere with cobalt detection by virtue of the characteristic blue color (of Cu) and green colors (Ni and Cr) of the ions themselves. When the amount of cobalt in solution is greater than any of the others, interference on the part of copper can be eliminated completely, while interference on the part of nickel and chromium can be reduced considerably. When excess thiourea is used, the copper on trituration with the reaction mixture forms a white complex with thiourea, while nickel and chromium are complexed to give pale green-yellow compounds. In this form copper does not interfere with cobalt detection at all. Nickel and chromium can be tolerated if the ratio Co:Ni:Cr is not less than 20:1:1; the sensitivity of the reaction is lowered to 1.4 μg cobalt.

2) Only bismuth interferes with the detection of cobalt when the method involving the soaking of dry thiourea with test solution, or the filter paper technique is employed.

3) With the exception of Bi^{3+}, Ni^{2+}, Cu^{2+} and Cr^{3+}, the remaining 26 elements listed above do not interfere with the proposed spot reaction for cobalt, nor do they lower the reaction sensitivity, independently of the ratio between their amounts and that of cobalt in their mixtures.

SUMMARY

1. A new spot test for cobalt is proposed which is based on the formation of colored compounds with thiourea.

2. Three techniques are outlined for carrying out this reaction for cobalt, in solids and in solution.

3. The selectivity and sensitivity of the reaction have been determined.

Received July 21, 1952.

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COPPER AS AN ABSORBENT FOR HALOGENS AND HYDROGEN SULFIDES FOR THEIR DETERMINATION IN AIR

P. M. Sadovsky

An essential drawback of the standard method of determining CO in the air of industrial premises for sanitary control, (GOST 5612-50)[1] is the instability of the baryta standard, which has accordingly to be checked daily under the experimental conditions (control test) and which leads to uncertainty and to a decrease in accuracy of the experimental results, especially for low CO concentrations in the air.

A study of the apparatus used for CO determinations under various conditions of heating the I_2O_5, throughput of air, and loading of the apparatus (with respect to CO concentration), enabled us to establish that one of the reasons for low baryta titers in the control test is the partial neutralization of baryta by iodine, since the latter is only weakly held by the potassium iodide, the iodine drawn through with the hot air into the baryta solution forms BaI_2 thereby lowering the titer. The fact that I_2 is transferred by the air stream from the potassium iodide solution into the baryta solution is easily confirmed: thus, if pure hot air is blown through the apparatus and a piece of starch paper is placed at the outlet tube from the KI absorption tube, then after a short time interval the paper starts to turn blue and becomes more intense the greater the amount of I_2 in the KI.

According to GOST 5612-50 metallic mercury can be used for absorption of I_2 instead of KI; the use of mercury is, however, not suitable for many reasons; on the basis of the similarity between the behavior of Hg and Cu towards halogens, therefore, we decided to use pure (electrolytic) copper in the form of turnings as an I_2 absorbent.

A preliminary test with copper as absorbent showed that the copper turnings completely and firmly held the I_2. Passage of dry air containing I_2 vapors through the copper turnings turns the copper black as the result of absorption of I_2 which is subsequently slowly reduced to form CuI, and the black color of the copper turns grey (CuI is white). If there is water vapor in the test air containing iodine the reduction of the iodine is rapid and the copper turnings are covered with a white layer of CuI.

Copper in damp air combines with atmospheric CO_2 to form a basic copper carbonate. According to our observations, pure copper turnings, on keeping for many weeks in test tubes under the micro climate of the laboratory did not combine with CO_2, and the hygroscopicity of the turnings was practically nil.

It follows naturally that copper turnings can be used for absorption of the other halogens as well as I_2.

Experiments in which air contaminated with H_2S was passed through copper turnings showed that H_2S could be completely absorbed with formation of CuS for a fairly rapid throughput of air, which would enable copper absorbents to be used for the determination of H_2S in air.

The copper absorbent is easily prepared: 8-10 g of pure copper turnings freed from dust by sieving through a silk sieve or by elutriation with ethyl ether are placed in a V-shaped tube with an internal diameter

[1] GOST = All-Union State Standard.

of 2-3 mm, the tube is stoppered with porous, fibrous asbestos, and the absorbent tube is ready. The tube is dried in a desiccator or in a drying oven at a temperature not greater than 100°, since CuO is formed at higher temperatures.

Metallic copper in the form of turnings or dust can also be used for the extraction of free halogens (as their respective copper salts) from their aqueous solutions.

We could not find any references to the use of metallic turnings for the absorption of gases and vapors in practical chemical analysis in the literature at our disposal.

Received May 20, 1953

DISCUSSION

THE ADDITIVITY OF REFRACTION DISPERSION AND A COMPARATIVE EVALUATION OF DISPERSOMETRIC METHODS OF DETERMINING AROMATIC HYDROCARBONS[1])

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In the article by B. A. Kazansky et al [1] it is suggested that a function of refraction dispersion which is an original combination of the well known Lorentz-Lorentz and Gladstone-Dahl formula:

$$\omega_R = \left[\left(\frac{n_F^2 - 1}{n_F^2 + 2} - \frac{n_C^2 - 1}{n_C^2 + 2}\right) : (n_D - 1)\right] \cdot 10^3.$$

be used for the determination of aromatic hydrocarbons.

The method suggested by Kazansky is very similar to the relative dispersion which we suggested, worked out, and published in a series of articles during 1946-1950 [2,3,4,5,6,7,8]. Our method is based on the use of the values $\omega_{FC} = \frac{n_F - n_C}{n_C - 1} \cdot 10^3$ or $\omega_{FCD} = \frac{n_F - n_C}{n_D - 1} \cdot 10^3$.

Before introducing this new method, one should carefully assess the experimental results obtained by both methods on the same materials and under identical conditions. Kazansky et al. [1], however, confined their references to our first paper [2], containing a description of an earlier variant of the method developed for use with an Abbe refractometer. The articles which followed and which were devoted to developing the method to make it more accurate, and also to check the method, are not mentioned at all. Even in 1946 we proposed, and subsequently described in detail [5,6,7], an improved variant of the method which we designed for accurate work with a Pulfrich refractometer requiring measurements of only two (and not three) refractive indices n_F and n_C. The use of ω_{FC} instead of ω_{FCD} or ω_R makes the relative dispersion method even more simple and convenient, since it requires only one source of light instead of two, and also cuts down the time required for carrying out measurements and calculations.

While keeping quiet about our recommendations re the use of ω_{FC} in dispersometric analysis and considering the comparative value of the functions ω_{FCD} and ω_R, B. A. Kazansky et al. [1] prefer the latter. The only basis for this preference is their affirmation that the values of ω_R for hydrocarbon mixtures follow the additivity rule better than ω_{FCD}, and consequently in the analysis of benzene and toluene fractions there is no need to introduce corrections for deviations from additivity.

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[1]) A discussion of an article by B. A. Kazansky, M. I. Rozengart, O. D. Sterligov, and G.A.Tarasov [1].

The conclusion re the strict additivity of ω_R in the work cited [1], is drawn on the basis of their own results for four systems and of a discussion of G. S. Pavlov's results for the system benzene-cyclohexane. Nevertheless G. S. Pavlov's very reliable results do not confirm the conclusion drawn in [1] re the additivity of ω_R, on the contrary they contradict it. The wrong interpretation of these results by Kazansky is apparently the result of mistakes in their calculations. Table 1 contains the results of our calculations which show that in the given system, the values of ω_R exhibit a systematic positive deviation from additivity, which is several times greater than the possible experimental error.

TABLE 1

Deviation of ω_R from additivity in the system benzene-cyclohexane

(Calculated from G.S. Pavlov's results [9])

Benzene content % weight P	Value of ω_R		Deviation of ω_R from additivity	ΔP in %
	Experimental	Additive		
0	92.0	–	–	–
4.61	95.5	95.3	+0.2	+0.3
10.09	100.3	99.3	+1.0	+1.3
15.69	104.9	103.4	+1.5	+2.1
20.11	107.1	106.6	+0.5	+0.7
25.18	111.2	110.3	+0.9	+1.2
29.98	114.8	113.8	+1.0	+1.3
35.38	119.1	117.7	+1.4	+1.9
37.21	120.3	119.0	+1.3	+1.8
45.09	126.1	124.7	+1.4	+1.9
49.58	129.2	127.9	+1.3	+1.8
54.90	133.1	131.8	+1.3	+1.8
60.04	137.1	135.5	+1.6	+2.2
65.33	140.5	139.4	+1.1	+1.5
70.21	144.6	142.9	+1.7	+2.3
74.76	147.5	146.2	+1.3	+1.8
80.16	150.6	150.1	+0.5	+0.7
84.96	154.5	153.6	+0.9	+1.2
90.19	157.8	157.4	+0.4	+0.6
94.96	161.1	160.8	+0.3	+0.4
100	164.5	–	–	–

The value of ΔP adduced in the last column of Table 1 characterizes the errors which arise during calculation of the benzene content by means of the additivity rule for ω_R. It is not difficult to see that their errors are always on the high side, and lead to inadmissible errors of 2-2.3% absolute. Our results for the system benzene-cyclohexane and also for 11 other systems containing aromatic hydrocarbons mixed with saturated hydrocarbons [6, 8, 10), as given in Table 2 are in complete agreement with the conclusion to be drawn from the results given in Table 1.

In each system we usually examined 4 mixtures with contents of aromatic hydrocarbons of 20, 40, 60, and 80% (roughly) which are designated in Table 2 by numbers in order of increasing aromatic hydrocarbon content. In order to economize on space in Table 2, only the values of the errors in aromatic content obtained by calculation according to ω_R by the method recommended in the article considered [1], are included. All the original results for these calculations are incorporated in our other papers [6,8,10].

TABLE 2

Errors in concentration of aromatic hydrocarbons when calculations are made on the assumption of the additivity of ω_R

Components of the mixtures	Errors (ΔP) in %			
	Mixture No. 1	Mixture No. 2	Mixture No. 3	Mixture No. 4
Benzene, cyclohexane [8]	+0.8	+2.2	+2.2	+1.5
Benzene, n-heptane [6]	+1.0	+2.0	+1.1	-
Benzene, 2,2,4-trimethylpentane[8]	+0.9	+2.0	+1.6	+1.7
Toluene, n-heptane [6]	+2.4	+2.2	+2.4	-
Toluene, methylcyclohexane [10]	+2.4	+2.8	+2.1	+2.5
Ethylbenzene, n-octane [10]	+0.3	+2.0	+2.2	+1.3
n-Xylene, n-octane [10]	+1.6	+2.4	+2.7	+1.1
Cymene, 2,2,4-trimethylpentane [8]	+1.6	+2.4	+2.0	+2.0
Mesitylene, 2,2,4-trimethylpentane [8]	+1.4	+2.2	+0.3	-0.5
Mesitylene, n-nonane [10]	+2.0	+2.3	+1.3	+1.8
Sec.-butylbenzene, sec.-butylcyclohexane [8]	+0.8	+1.4	+1.0	±0.0
Sec.-butylbenzene, diisoamyl [8]	+0.6	+1.1	+1.8	+1.2

It obviously follows from these results that ω_R has no advantages over relative (ω_{FCD}, ω_{FC}) or even specific (δ_{FC}) dispersion with respect to additivity. In these systems a systematic deviation of ω_R from additivity is observed, which leads to enhanced values for the aromatic content of from 2-2.5% absolute. For exact analytical work this deviation is the same as for the methods involving specific and relative dispersion [6,8].

Thus the only reason advanced for preferring ω_R [1], to ω_{FC} and ω_{FCD} falls to the ground.

The decisive factor in deciding the advantages of one or another variant of the dispersometric method is a direct comparison of the results obtained by these variants on the same materials. We have at our disposal results of such a comparison; these are given in Table 3.

Synthetic mixtures of benzene and toluene with dearomaticized benzene fractions were prepared and examined as described previously [6,8]. The aromatic hydrocarbons used have also been described before [8,10].

Table 3 contains results obtained using a Pulfrich refractometer, and the respective methods of relative dispersion ω_{FC} [6], specific dispersion δ_{FC} [11], and the method of Kazansky et al. [1]. All calculations were made using the mean value of the dispersion of the saturated hydrocarbons indicated by the respective authors [6, 11, 1]. For the methods of relative dispersion ω_{FC}, and specific dispersion δ_{FC}, in accordance with the author's method, corrections of non-ideality of ω_{FC} and δ_{FC} were applied for the benzene and toluene mixtures by means of tables[1]).

The results obtained demonstrate the superiority of the ω_{FC} [6] method over other dispersometric methods of determining aromatic hydrocarbons: not only is this method simpler, it is also more accurate. Method ω_R [1], gives much poorer results. Errors obtained when calculating the results according

[1]) We should like to take this opportunity to correct an error in article [6]: $P_{corr.}$ was printed instead of P on p.241 in the line following formula (8).

TABLE 3
Results of analyses of benzene and toluene mixtures by dispersometric methods

Components of mixtures	Aromatic content %	Method ω_{FC} [6]		Method δ_{FC} [11]		Method ω_R [1]	
		found %	error %	found %	error %	found %	error %
Benzene, dearomaticized, fraction 50-95°	53.5	53.9	+0.4	54.3	+0.8	56.7	+3.2
Benzene, dearomaticized, fraction 50-95°	31.7	31.0	-0.7	31.3	-0.4	32.8	+1.1
Benzene, dearomaticized, fraction 50-96°	19.6	19.1	-0.5	19.4	-0.2	22.2	+2.6
Benzene, dearomaticized, fraction 50-95°	11.0	12.2	+1.2	12.8	+1.8	15.0	+4.0
Toluene, dearomaticized, fraction 95-122°	46.3	46.6	+0.3	45.3	-1.0	48.5	+2.2
Toluene, dearomaticized, fraction 95-122°	30.2	31.0	+0.8	29.3	-0.9	33.1	+2.9
Toluene, dearomaticized, fraction 95-122°	22.1	22.4	+0.3	20.5	-1.6	24.2	+2.1
Toluene, dearomaticized, fraction 95-122°	15.1	15.2	+0.1	13.1	-2.0	17.4	+2.3
Mean deviation . . .			0.5		1.1		2.5

to ω_R are on the high side for P, and are often inadmissibly high. These errors are no doubt caused to a considerable extent by disregard of the deviations of ω_R from additivity.

Another reason for the considerable errors of method ω_R is the comparatively large variation in the values for saturated hydrocarbons. Calculations using the same experimental results and using the actual values of ω_R for the dearomaticized fractions tested lead to a decrease in the mean deviation to 1.5%, but the systematic character of the error is maintained. By taking into account the deviation of ω_R from additivity it would be possible to improve the results even more, but, whatever corrections are applied we fail to see why ω_R should be preferred to ω_{FC}.

In conclusion we should like to point out that it is incorrect to say as in [1], that the method of relative dispersion was proposed by us in 1946 a "year later" than Mokhnatkin [12]. Our first paper [2] which contained the basis of the relative dispersion method, together with results obtained on the Abbe refractometer confirming its use, was reported at Acad. Sci. USSR November 1, 1944, and was received by the editorial board of J. Gen. Chem. on April 1, 1945.

In Mokhnatkin's review [12] which was published in May 1945 there is only a brief mention that a method was being worked out in the laboratory of the "Khimgaz" factory, for analysis of gasolines, using relative dispersion. No results of this work have as yet appeared in the literature.

SUMMARY

1. The values of ω_R for mixtures of aromatics, paraffins or naphthenes show a systematic deviation from additivity which usually exceeds the possible

experimental error.

2. Disregard of this deviation of ω_R from additivity may lead to errors of the order of 2-2.5% absolute in dispersometric analysis.

3. A method of determining aromatic hydrocarbons by means of ω_R which was only suggested recently [1], has no real advantages over the relative dispersion method ω_{FC} [6] and is not as accurate as the latter.

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[1] See Consultants Bureau Translation, p. 275.

[2] See Consultants Bureau Translation, p. 359.

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NEW REAGENTS

OXIDATION-REDUCTION INDICATOR

"FERROIN"

The Institute of Chemical Reagents has issued a new oxidation-reduction indicator - ferroin - which is a complex salt of orthophenanthroline and ferrous oxide $Fe(C_{12}H_8N_2)_3SO_4$, molecular weight 692.5.

The oxidation-reduction potential of ferroin is 1.06 V.

The normal oxidation-reduction potential of ferroin changes with pH (Smith and Richter 1944).

Molar concentration of sulfuric acid	1	2	3	4	6	8
Potential in volts	1.06	1.03	1.00	0.96	0.89	0.76

On oxidation, the Fe^{2+} phenathroline complex changes over to the Fe^{3+} complex

$$[Fe(C_{12}H_8N_2)_3]^{2+} \rightleftharpoons [Fe(C_{12}H_8N_2)_3]^{3+} + e$$

and the red color changes to pale blue.

The use of ferroin as a reduction-oxidation indicator has been discussed in a review article: G. A. Pevtsov, Proc. All Union Conference on Analytical Chemistry, Vol. IV, 1948 and also in Kolthoff and Sandel's book "Quantitative Analysis" State Chem. Press 1948.

The use of ready made ferroin is far more convenient than the preparation of a solution of ferroin in the laboratory from orthophenanthroline and ferrous sulfate.

"Ferroin" is issued by Glav. Khim. Reaktiv. (State Chemical Reagents).

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CHROMATOGRAPHIC METHODS IN QUALITATIVE ANALYSIS II

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Ion-exchange chromatography, which was proposed and developed by the Soviet scientists E.N. Gapon and T.B. Gapon [1], is one of the variants of M.S. Tsvet's adsorption chromatography [2].

The basis of ion-exchange chromatography is exchange of an adsorbed cation for an ion contained in the adsorbent [3]. When chromatographic aluminum oxide is used as the adsorbent, e.g., the formation of a chromatogram of cations is the result of differences in exchange intensities of the cations in the test solution for the sodium ions in the aluminum oxide aluminate [4].

If several cations are present in solution, then the cation with the greatest adsorbability will be concentrated in the upper part of the column, and displaces cations with lower adsorbability, which will be accordingly located in the lower part of the column.

Material collected in drawing up adsorption series of cations and anions according to their adsorbability on various adsorbents for each analytical group taken separately, was adduced in our first paper [5].

The aim of the present paper was the development of qualitative chromatographic analysis of 4th group cations on chromatographic aluminum oxide.

Adsorption series of fourth group cations are arranged on various adsorbents in the order shown in Table 1.

TABLE 1

Adsorbent	Color of adsorbent	Adsorption series
Chromatographic aluminum oxide aluminate	White	$Bi^{3+} > Hg_2^{2+} > Hg^{2+} > Pb^{2+} > Cu^{2+} > Ag^{+} > Cd^{2+}$
Sodium permutite	White	$Hg_2^{2+} > Hg^{2+} > Ag^{+} = Pb^{2+} > Cu^{2+} = Cd^{2+}$
Suifunite	Pale yellow	$Hg_2^{2+} > Hg^{2+} = Bi^{3+} = Pb^{2+} > Ag^{+} > Cu^{2+} > Cd^{2+}$
Askangel	White with a greyish shade	$Hg_2^{2+} = Ag^{+} > Hg^{2+} > Pb^{2+} > Cd^{2+} > Cu^{2+}$

Before developing the chromatograms with various reagents it was essential to find out the color of the adsorbed cations on the adsorbents. A solution of the test cation or mixture of test cation was accordingly passed through the adsorbent column. The results obtained are given in Table 2.

TABLE 2

Cations	Color of zone on the adsorbents			
	Chromatographic aluminum oxide	Permutite	Suifunite	Askangel
Hg_2^{2+}	Pale yellow zone with a grey strip	Yellow-green zone with a grey strip	Colorless	Colorless
Hg^{2+}	Pale-orange zone with a rose tint	Orange zone with a grey ring (contaminated with Hg_2^{2+})	Colorless	Colorless
Cu^{2+}	Blue	Bright blue	Bluish green	Green
Pb^{2+}, Ag^{+}, Cd^{2+}, Bi^{3+}	All cations form colorless zones on the adsorbents			
$Cu^{2+} + Hg^{2+}$	Above, rose strip; below, blue strip	Above, orange ring; below, blue strip	Bluish-green zone	Pale green zone
$Cu^{2+} + Hg_2^{2+}$	Above, pale-yellow zone with a grey strip; below, blue zone	Above, yellow-green zone with a grey strip; below, blue	Bluish-green zone	Pale green zone
$Hg_2^{2+} + Hg^{2+}$	Yellow zone with a grey strip, Hg_2^{2+}; below Hg^{2+} in the form of a yellow zone	Yellow	Colorless	Colorless
$Hg_2^{2+} + Pb^{2+} + Ag^{+}$	Yellow-green zone with a grey strip	Yellow-green zone with a grey strip	Colorless	Colorless
$Cd^{2+} + Cu^{2+} + Bi^{3+} + + Hg^{2+}$	Blue zone	Blue zone	Bluish-green	Pale green
Mixture of all Group 4 cations	Above, pale yellow zone of mercury; below, blue zone of Cu^{2+}	Above, yellow color; below, blue zone of Cu^{2+}	Bluish-green	Colorless

These results show that the cations Hg^{2+}, Hg_2^{2+}, and Cu^{2+} can be detected directly on the adsorbent; in order to detect the remaining cations they must be developed further according to the following method. The test solution, composed of equal volumes of solutions of the cations of the 4th analytical group of equal concentration, is placed on the chromatographic column with d = 0.5, h = 10 cm, containing the adsorbent, by means of a pipet. The chromatogram is washed with 2-3 drops of water, after which the developer is introduced into the column. The adsorbed cations which are located in different zones of the chromatogram react with developer to form colored chemical compounds.

Experiments were made on chromatographic aluminum oxide, sodium permutite, and suifunite. When the test solution was passed through bentonite-askangel, reaction between adsorbent and salt solution, the pH of which was 0.79, occurred; no experiments were carried out, therefore, on the formation of cation chromatograms on bentonite-askangel.

Chromatograms of Fourth Group Cations Developed with Potassium Iodide

1. A solution of the mixture of cations Hg_2^{2+}, Pb^{2+}, and Ag^+ was passed through the adsorbent, and after washing with water the chromatograms were developed with two-normal potassium iodide. Results are adduced in Table 3.

TABLE 3

Expt. No.	Adsorbent	Appearance of the developed chromatogram (from top to bottom of the column)
1	Chromatographic aluminum oxide	Dark green zone of Hg_2I_2 Yellow zone of PbI_2 with a narrow, bright red zone of HgI_2, which disappears in excess reagent with formation of the colorless complex $[HgI_4]^{2-}$. Pale yellow zone of AgI
2	Suifunite	Black zone with a green shade of Hg_2I_2, yellow PbI_2 with a narrow bright red zone of HgI_2 No yellow zone of AgI was visible
3	Sodium permutite	Brownish-black zone of the mixture of the cations Hg_2^{2+} and Ag^+, and below the bright yellow zone of PbI_2

A comparison of the chromatograms in the experiments described above shows that the best one is that formed on chromatographic aluminum oxide, by means of which it is possible to detect all the cations simultaneously, though the brightest colors are given on sodium permutite. The narrow, bright red zone of HgI_2 is formed as a consequence of the fact that mercurous salts usually contain the Hg^{2+} ion. The red zone of HgI_2 disappears on passing excess potassium iodide, as a result of formation of the colorless complex $[HgI_4]^{2-}$. Silver ions could not be detected on suifunite or permutite (Experiments 2 and 3) so that these adsorbents are not suitable for detection of Ag^+, Pb^{2+}, and Hg_2^{2+}. Tests were also made by the above method of the effect of cation concentration on their detection in solution. Solutions containing from 0.3 to 0.001 g-equiv./liter were used. The results of these experiments show that the cations could be detected at 0.005 N concentration for each of them. Hg_2^{2+} cations could be detected with potassium iodide at even lower concentrations.

2. A 0.3 N solution of a mixture of Cu^{2+}, Hg^{2+}, Bi^{3+}, and Cd^{2+}, was passed through the adsorbent; after a water wash the chromatogram was developed with a 2 N solution of potassium iodide (Table 4).

The results obtained indicate a possibility of detecting the cations Bi^{3+}, Cu^{2+}, Hg^{2+} with potassium iodide when they all occur together in solution. Cd^{2+} cations have to be detected by another developer. On development with potassium iodide the bismuth cations form a black zone of BiI_3, which gradually dissolves in excess reagent to form the complex $[BiI_4]^-$, which is yellow or orange in color (Expt. 1). On development with potassium iodide, Cu^{2+} forms CuI_2, which is transformed into CuI according to an oxidation-reduction process:

$$2CuI_2 \longrightarrow 2CuI + I_2.$$

The iodine evolved forms a brown zone below the chromatogram.

TABLE 4

Expt. No.	Adsorbent	Appearance of the developed chromatogram (from top to bottom)
1	Chromatographic aluminum oxide	Black zone of BiI_3 merging into grey and then into an orange-yellow color; this is followed by a bright red zone of HgI_2, and a greenish-blue zone of Cu^{2+}, below a brown zone of I_2.
2	Suifunite	Pale yellow zone with a narrow bright red band of HgI_2, followed by a black BiI_3 zone and a blue Cu^{2+} zone, below which is the brown zone of I_2.
3	Sodium permutite	The chromatogram is analogous to that in Expt. 1. The color of the zones is brighter and the zone boundaries more sharply defined.

The best chromatograms from the point of view of color brightness of the zones are those formed on sodium permutite.

3. A 0.3 N solution of the mixed cations of Group IV was passed through the adsorbent and the chromatogram developed with 2 N potassium iodide, after water washing. The results obtained are given in Table 5.

TABLE 5

Expt. No.	Adsorbent	Appearance of the developed chromatogram (from top to bottom)
1	Chromatographic aluminum oxide	Black zone of BiI_3 merging into yellow. Followed by a dark green zone of Hg_2I_2 and a bright orange zone of HgI_2. Next a blue zone ending in a layer with a brown color (from the iodine evolved).
2	Suifunite	Dark green zone of Hg_2I_2 followed by an orange strip with a brown shade of Bi^{3+} and below a bright orange zone of HgI_2. The bottom of the column was colored brown by the iodine evolved.
3	Sodium permutite	Green zone of Hg_2I_2 with a bright red HgI_2 band, below which there is a dark orange BiI_3 zone. This is followed by a blue Cu^{2+} zone and a brown zone from iodine evolved. After 24 hours the zones' colors were brighter.

The results given in Table 5 show that by using potassium iodide as the developer the following cations of Group IV can be detected: Hg_2^{2+}, Hg^{2+}, Bi^{3+}, and Cu^{2+}. Pb^{2+} and Ag^{+} cations are not detected by potassium iodide in a solution of a mixture of fourth group cations, since the yellow color of their iodide compounds is masked by the yellow of the bismuth complex and by the free iodine evolved. In the absence of Bi^{3+}, Pb^{2+} ions can be detected in the form of a yellow zone of PbI_2.

Chromatograms of Fourth Group Cations

Developed with Hydrogen Sulfide Solution

An equimolar solution of the mixed cations Hg^{2+}, Cu^{2+}, Bi^{3+}, and Cd^{2+} was passed through a 4-6 cm column of chromatographic aluminum oxide; after washing with water the chromatogram was developed with a hydrogen sulfide solution. Chromatograms were developed for 30 minutes. The appearance of the chromatograms was as follows: above – the brown colored zone of Bi_2S_3, followed

by a black zone of mercuric sulfide; below this a grey zone of copper, and still lower – a pale yellow cadmium zone. By means of such a chromatogram it is possible to detect cadmium in the presence of other cations.

On passing a hydrogen sulfide solution through a column on which is already adsorbed a mixture of all fourth group cations, the following chromatogram was formed: on top – a bismuth brown zone, then a black mercury zone, and then a dark grey lead zone. After the lead zone there was a grey blue copper zone and finally a dark grey silver zone.

At the bottom of the chromatogram a yellow cadmium zone was formed. Development lasted on an average 50-80 minutes. Tests were made with solutions containing Cd^{2+} ions and concentrations of 0.1 to 0.001 g-equiv./liter. Cadmium ions were clearly detected in all the zones. In the last instance at a concentration of 0.01 g-equiv./liter there was a brighter coloration of the yellow cadmium zone.

Additional experiments were made on the detection of cadmium cations in the presence of copper cations. In this case a mixture of cadmium and copper ions, 0.1 N with respect to each, was passed through an aluminum oxide column; the chromatogram was washed with water and developed with hydrogen sulfide. A brown copper zone was formed on top; this was succeeded by a mixed brown zone of copper and cadmium cations, and finally, on the bottom, a bright yellow cadmium zone.

On passing a solution of the mixed cations Hg^{2+}, Bi^{3+}, Cu^{2+}, and Cd^{2+} through suifunite, and subsequently developing the chromatogram with hydrogen sulfide, two zones were formed: a dark zone of black sulfides, and below – a dirty yellow cadmium zone.

On passing the same solution through permutite and subsequently developing the chromatogram with hydrogen sulfide, one uniform black zone was formed; no yellow cadmium zone was obtained. The chromatogram confirmed the correctness of the adsorption series of fourth group cations on permutite, on which the copper ions have equal adsorbability to cadmium.

The best chromatograms were obtained on chromatographic aluminum oxide, on which bismuth ions were readily detected in the form of a brown zone, and the cadmium ions in the form of a yellow zone. Similar chromatograms were formed when sodium sulfide solution was used for developing.

The use of gaseous hydrogen sulfide cuts down the development time. On sucking gaseous hydrogen sulfide through a chromatogram of fourth group cations, a bright yellow zone of cadmium sulfide is formed in a matter of minutes.

Chromatograms of Fourth Group Cations Developed with Alkali Solution

A solution of mixed cations of the fourth group was passed through a chromatographic aluminum oxide column. 2 zones were formed: a yellow zone with a grey-violet border of mercury, and below a blue zone of copper ions. The chromatogram was washed with water and then developed with a 2 N solution of alkali. On top a grey zone of mercury ions in the form of Hg_2O was formed which merged into a yellow HgO zone; this was followed by a blue ($Cu(OH)_2$) zone and a brown silver zone. The silver zone gradually darkened and acquired the dark brown color characteristic of Ag_2O.

The best chromatogram was the one of Group IV cations obtained on passing their solution through a column of chromatographic aluminum oxide given a preliminary wash with an alkali solution. The zones obtained for the mercury, copper, and silver ions were more clearly defined. Silver can be readily detected in the presence of other cations by the use of alkali.

Chromatograms of Group IV Cations Developed with Sodium Stannite and Thiourea Solutions

A solution of Group IV cations was passed through a chromatographic aluminum oxide column and the chromatogram developed with sodium stannite; 2 zones were formed: on top – a grey zone of Bi^{3+} ions in the form of reduced metallic bismuth; this was followed by a black zone of Hg^{2+} ions as metallic mercury. The color of the other zones remained unchanged. Through a second column of the adsorbent containing adsorbed Group IV cations, a solution of thiourea was passed. A yellow bismuth zone was formed, and below this a black zone of Hg^{2+} formed; the other ions were not developed.

On the basis of the experiments described above two methods for the qualitative chromatographic analysis of Group IV cations were worked out: 1) using stannite; 2) using thiourea.

A Chromatographic Method for the Detection of Group IV Cations by Means of Stannite

A 2 N solution of alkali is passed through a column of chromatographic aluminum oxide; this is followed by 5-6 drops of the test solution of a mixture of Group IV cations. Three zones are formed: on top – a mixed zone of Hg^{2+} ions with a yellowish tinge of Hg^{2+} ions in the form of HgO; this zone is followed by a blue copper zone, and, finally, a brown Ag_2O zone. After washing with water to detect Bi^{3+} and Hg^{2+}, the chromatogram is developed with sodium stannite. A grey zone is formed as the result of separation of metallic bismuth according to the reaction:

$$2Bi^{3+} + 3Na_2SnO_2 + 6NaOH = 2Bi + 3Na_2SnO_3 + 6Na^+ + 3H_2O;$$

below this zone there is a black zone of Hg^{2+}.

On developing the chromatogram with potassium iodide, mercury is detected in the form of a bright orange band of HgI_2; after 2-3 minutes a yellow zone of lead iodide appears which is distinguishable by the characteristic luster of PbI_2 crystals. Cadmium is detected in another column by means of gaseous hydrogen sulfide. By means of this method all group IV cations can be detected in 7-8 minutes. Experiments were made to study the effect of solution concentration on the detection of cations by the above method. The cations Pb^{2+}, Cu^{2+}, Hg^{2+}, Ag^+ are easily detected in 5 drops of solution for a concentration of 0.01 g-equiv./liter; Hg^{2+} can be detected at an ionic concentration of 0.00026 g-equiv./liter while Bi^{3+} cations can be detected at an ionic concentration of 0.00007 g-equiv./liter.

A Chromatographic Method for the Detection of Group IV Cations by Means of Thiourea

Three columns containing chromatographic aluminum oxide are prepared. Through one column 2-3 drops of test solution are passed and the chromatogram developed with thiourea. The appearance of a yellow zone indicates the presence of bismuth ions.

The formation of a black zone below the yellow one signifies the presence of mercury ions [1]. 2-5 drops of 2 N alkali are passed through the second chromatographic column, followed by 2-5 drops of test solution.

Three zones are formed; on top – a yellow zone of mercury ions as HgO, followed by a blue zone of $Cu(OH)_2$, and below that a brown zone of Ag^+. The chromatogram is next developed with potassium iodide. On top, a black-yellow zone of bismuth in the form of BiI_3 soluble in excess reagent, is formed; the mercury zone [1] acquires a greenish ting of Hg_2I_2; below this, a bright orange zone of Hg^{2+} as HgI_2 forms, together with a yellow lead iodide zone.

The bottom of the column is colored brown from the I_2 evolved. In the presence of bismuth ions, which are easily detected in the first column by means of thiourea, the lead cannot always be detected in the second column, because the complex $[BiI_4]$, which has a yellow color, may mask the yellow color of lead iodide. In such cases it is better to detect lead by the first method, viz., the stannite one. Stannite reduces bismuth ions to the free metallic state, so that lead can then be detected in the form of yellow PbI_4 by using potassium iodide.

Cadmium is detected in the third column. 3-4 drops of the test solution are passed through the column; gaseous hydrogen sulfide is then drawn through the adsorbent. A yellow CdS zone forms at the end of the column in a matter of seconds.

All the chromatographic analyses can be carried out in 5-7 minutes by using this technique.

Experiments were carried out to study the effect of solution concentration on the detection of Group IV cations by this method. Group IV cations could be detected in 5 drops of solution at the concentration limits of:

Bi^{3+} cations on development with thiourea at 0.00025 g-equiv./liter.

Hg_2^{2+} cations on development with thiourea at 0.004 g-equiv./liter.

Hg^{2+} cations on development with potassium iodide at 0.008 g-equiv/liter.

Ag^{+} cations on development with alkali at 0.008 g-equiv./liter.

Cu^{2+} cations by detecting their blue color on the adsorbent at 0.017 g-equiv./liter.

Cd^{2+} cations on development with gaseous hydrogen sulfide at 0.01 g-equiv./liter.

Supplementary experiments were made in order to compare the characteristics of various qualitative methods of detecting Group IV cations in solution.

A solution of a mixture of Group IV cations was analyzed by four methods: a macro and a semi-micro method (Alekseev's method), a spot test technique (Tananaev), and the chromatographic method.

The results of these tests, which are given in Table 6, show that the chromatographic method possesses several advantages over the others. 5-7 minutes only are required for a chromatographic analysis, while 2.5 hours is necessary for the classical macromethod, and from 40 minutes to 1 hour 50 minutes for the other methods. The amount of reagents used for chromatographic work is less. E.g., in order to analyze 5 ml of test solution by the classical method, the following amounts of reagents were used: 4.5 ml of 2 N HCl, 8 ml of 2 N H_2SO_4, 5 ml of 2 N HNO_3, 8 ml of 2 N NH_4OH, etc., while for chromatographic analysis fewer reagents are needed, and the ones used are only in amounts of ca. 0.2-0.3 ml, i.e., 20-40 times less than that required for macro and semimicro analysis. The amount of test solution required for analysis by the chromatographic method is less than that required for any of the other methods. The smallest volume that can be conveniently dealt with by the macro method is 5 ml, and if this volume is cut down further, the analysis becomes more difficult to carry out, while increasing the volume leads to an increase in the amount of reagents employed, and to a longer time of analysis.

Results of Experiments 3, 5 6, 8, 9, and 12 (Table 6) show that the chromatographic method is also the most sensitive method of the ones tried. While the macro, semimicro, and spot test methods only enabled all the cations to be detected at a concentration of 0.0317 N, a concentration of 0.0078 N could be easily detected by the chromatographic method for all the test cations.

TABLE 6

Expt. No.	Method	Equimolar concentration	Amount of test solution used for analysis, ml	Time to carry out analysis, minutes	Results of the analysis
1	Macro method	0.0625	5.0	165	All the cations were easily detected
2	"	0.0312	5.0	150	"
3	"	0.0156	5.0	145	Hg_2^{2+}, Hg^{2+} and Ag^{+} were detected. The remaining cations were not detected
4	Semi-micro method	0.0625	1.0	100	All the cations were easily detected
5	"	0.0312	1.0	110	All the cations were easily detected except Bi^{3+}
6	"	0.0156	1.0	90	All the cations were easily detected except Cd^{2+} and Bi^{3+}
7	Spot-test method	0.0312	1.1	40	All the cations were easily detected except Cd^{2+}
8	"	0.0156	1.0	40	All the cations were easily detected except Bi^{3+} and Cd^{2+}
9	"	0.0078	1.0	35	All the cations were easily detected except Pb^{2+}, Bi^{3+}, and Cd^{2+}
10	Chromatographic method	0.0625	0.7	6	All the cations were easily detected
11	"	0.0312	0.7	7	"
12	"	0.0156	0.7	5	"
13	"	0.0078	0.7	6	All the cations were easily detected except Hg^{2+}. The formation of a Hg^{2+} zone must be looked for immediately after passing through a solution of KI.

SUMMARY

1. The possibility has been demonstrated of detecting Group IV cations when they all occur simultaneously in solution by adsorption on: chromatographic aluminum oxide, sodium permutite, and suifunite, using various developers:

a) using potassium iodide as developer, the following cations can be detected: Hg_2^{2+}, Hg^{2+}, Cu^{2+}, Bi^{3+}, and also Pb^{2+} in the absence of Bi^{3+};

b) the use of a hydrogen sulfide solution or sodium sulfide, or gaseous hydrogen sulfide can lead to the detection of Cd^{2+} on chromatographic aluminum oxide and suifunite. The possibility of using gaseous hydrogen sulfide

as a developer has been demonstrated;

c) an alkali developer detects: Hg^{2+}, Hg_2^{2+}, CuI^{2+}, Ag^{+};

d) by using thiourea and stannite, HgI_2^{2+} and Bi^{3+} can be detected.

2. The effect of cation concentration in solution and the detection of Group IV cations on chromatographic aluminum oxide using various developers has been studied. When potassium iodide is used all the cations can be detected at a concentration of 0.005 N, while cations of Hg_2^{2+} can be detected at even lower concentrations; when hydrogen sulfide is used the cadmium can be detected at a concentration of 0.01 N.

3. Two methods involving the use of stannite and thiourea have been worked out for the qualitative chromatographic analysis of Group IV cations when they occur simultaneously in solution. The limiting concentrations of the various cations which can be detected chromatographically have been determined. The methods involving stannite and thiourea can detect these cations at a concentration of 0.01 N.

Hg_2^{2+} and Bi^{3+} can be detected with stannite and thiourea at even lower concentrations.

4. Four methods of detecting Group IV cations in solution have been compared: a macro method, a semi-micro method, a spot-test method, and the chromatographic method. The chromatographic method is the best because: 1) it enables all the cations to be detected in solution in 6-7 minutes; 2) only small amounts of reagents are required, and lengthy operations such as filtration, heating, precipitation, and other operations encountered during normal analysis are eliminated; 3) the volume of test solution is smaller than that required for any of the other methods, and the cations can be detected at lower concentrations. The chromatographic method is the most sensitive of those tried.

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THE PART PLAYED BY DIFFUSION IN THE PROCESSES WHICH OCCUR ON THE ELECTRODES DURING SPECTRAL ANALYSIS USING SPARK EXCITATION

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At the present time the search for radical methods of combating "third element" effects is one of the fundamental problems of spectrochemical analysis. Taking into account the effect of third elements by constructing systems of parallel curves, and making numerous series of standards, etc., is only a half-measure, which does not satisfy contemporary requirements, both in view of the complexity of the methods involved, and also because these methods are not accurate enough.

A search for radical methods of combating third element effects is, however, impossible until a theory has been worked out which can explain quantitatively all the known cases of this effect. At the present time the most popular theory is that of L. N. Filimonov [1,2], who connects the effect of third elements with sparking processes, and explains both these phenomena as processes of selective oxidation which occur on the electrode surface. Filimonov, by means of examples, convincingly explains both the shape of the sparking curves and third element effects. Filimonov's theory, however, cannot explain all the variety of known facts connected with the third element effect. Of particular importance is the fact that the basic practical conclusion to be drawn from Filimonov's theory on the question of combating the effect of third elements is in direct contradiction with everyday analytical practice. According to Filimonov's theory, the effect of third elements should cease if the test material is completely oxidized or is converted into a stable salt, since in such a case the processes of selective oxidation come to a stop on the electrode surfaces. A number of examples can be adduced which show that converting the test material to the oxide or to a salt does not prevent third element effects. A. G. Komarovsky [3], while developing a method for the determination of calcium in high alloy steels, dissolved the test material, then soaked the needle electrodes with its solution, dried the electrodes, and then subjected them to a Raisky spark discharge. It turned out in this case that the presence of third elements showed a very pronounced effect on the determination of calcium. Azcona and Martin [4] found that Sn and Pb displayed very marked mutual effects on salts of the system Zn – Sn – Pb, solutions of which were placed on the needle electrodes and dried (excitation by a Feisner spark). It is of interest to note that the effect of Pb on the results of Sn determinations while working with salts of the metals is much more clearly defined than during analysis of metallic samples of similar composition.

We found a very marked mutual effect shown by certain elements on the analytical results of slag analysis. In this case tablets pressed from powdered slag and copper were analyzed, analysis was commenced 1.5 minutes after preliminary sparking. When this method is employed the sparking spot is a continuous black surface. Measurement of the electrical resistance of the film and microscopic examination showed that the copper is completely oxidized under these conditions to CuO. When slag is analyzed in tablet form, therefore, the material is transformed into vapor from a completely oxidized film.

In all the three cases just considered, no selective oxidation occurs on the electrode surfaces during the analytical exposure time; nevertheless,

there is a clearly expressed third element effect.

We consider that it is impossible to explain third element effects simply by oxidation-reduction processes which occur on the electrode surfaces; the part played by diffusion must be taken into account. Filimonov [1], rightly points out that under the action of a spark discharge, heating of the surface layer and adjacent layers occurs, and this activates diffusion processes. It is, however, not only a question of the activation of diffusion processes; another essential factor is that the value of the diffusion coefficient depends on third element effects, as is well known from the physics of solid bodies. Thus, third element effects must be looked upon as being the result of two processes: selective oxidation on the electrode surface on the one hand, and changes in the diffusion coefficients which occur under the influence of third elements.

Let us consider in detail the experimental and theoretical material available on the question of diffusion in solids and liquids.

It is usually assumed that diffusion in solid bodies follows the space-time diffusion equation:

$$\frac{dc}{dt} = \text{div } (D \text{ grad } c), \qquad (1)$$

where c is the concentration of the diffusing atoms; D is the diffusion constant.

It has been established experimentally that at a given concentration, D depends on the termperature as follows:

$$D = D_0 e^{-\frac{\epsilon}{RT}}; \qquad (2)$$

where ϵ is the activation energy of the so-called heat of disintegration; R is the Universal Gas Constant; D_0 a factor which is independent of temperature.

According to the work of S. Gertsriken and I. Dekhter [5], Eyring and Van Johnson's formula is the one with the best physical basis for the factor D_0.

$$D_0 = e^{\frac{\Delta S}{R}} \left(\frac{kT}{h}\right) \frac{d^2}{2.72}, \qquad (3)$$

where ΔS is activation entropy; R – the gas constant; k the Boltzman constant; h Planck's constant; d the shortest interatomic distance; and T is the absolute temperature.

The presence of a third element essentially affects the value of the diffusion coefficient. S. Gertsriken, A. Geller, and V. Trofimenko [6] studied the effect of Sn, Ni, and Pb on the diffusion of Zn in α-brass. It was shown that even 0.5% Sn increases the diffusion of Zn 5 times; change of Sn content from 2 to 2.5 increases the diffusion of Zn from 10-12 times. 2.1% Ni shows no appreciable effect; on increasing the Pb content from 0.13 to 3.55 the diffusion coefficient increased from 6-15 times. Grube and Jedele [7], found that 0.5% Mn in nickel decreases the diffusion of copper at 1025° to a third. Bungardt and Bollenrath [8] established that 2.7% of zinc in a Mg-Al alloy halves the diffusion coefficient of Mg in Al. Diffusion in dielectrics has not been studied to such an extent as in metals, but the same type of phenomenon happens here also. Fig. 1 is a graph taken from a paper by Shvartsman, Gruzin, and Pechenev [9], which shows the relation between log D and 1/T for iron in magnesite and chromomagnesite. Here the third element – chromium – shows a considerable effect on the diffusion coefficient of iron.

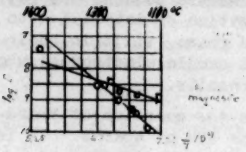

Fig. 1. Relation between log [D] and 1/T [9].

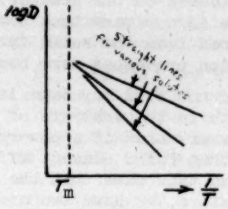

Fig. 2. Straight lines for different compounds [10]. T_m = melting point.

In the case of liquids, the picture is totally different.

In liquids the diffusion coefficients of different components are practically the same as for the particles of liquid itself. Fig. 2 represents a graph of Bugakov's which we have borrowed from Frenkel's book [10], which shows that for various solutes in the same solid phase, straight lines with differing slopes ($\tan \alpha = \epsilon/R$) are obtained; all these lines fan out from the melting point of the basic element itself. Consequently, at the melting point the diffusion of the various components becomes practically equal, and remains so in the melt.

It is possible to explain quantitatively all the cases of third element effect known to us which crop up during spark excitation, from the point of view of theories which have been developed and from actual results, both taken from papers on the physics of solid bodies.

1. Third element effects during the analysis of salt precipitates on electrode needles, and during the analysis of slags in the form of tablets, which cannot be explained by Filimonov's oxidation-reduction theory, can be explained easily by changes in the diffusion coefficient under the influence of third elements.

2. From the theory of the solid state one would expect third element effects to disappear on switching over from solid to liquid electrodes. Actually the papers of Rusanov et al [11, 12, 13], Borovik and Borovik-Romanova [14], Delaney and Owen [15], and also our own work on the analysis of slags in aqueous solutions, show that if the transformation to the vapor phase takes place from a liquid phase, then third element effects are not observed for ordinary concentration ratios of test element and third element. When working with solutions, third element effects only appear when the concentration of third elements becomes about twice or more that of the test element. In this case, the effects are apparently not related to the transformation of the material from the electrode to a vapor, but to processes which occur in the plasma.

As mentioned above, during spectrographic analysis of slags in the form of tablets and involving the use of a spark we discovered very marked third element effects; they disappeared completely when the test material was dissolved. Consequently, in tablets the third element effect was connected with diffusion processes on the electrodes and not with plasma processes (selective oxidation on the surface of the tablets cannot play an essential part, since all the components of the slag are completely oxidized). On switching over to solutions, third element effects become so small that from the graphs constructed for slag standards it is possible to analyze slags as widely different as lime, dolomite, magnesite, iron ore, etc. Such analytical methods are completely out of the question when the test material is in solid form during analysis.

We did not find that Sn and Pb showed mutual effects during analysis of

non-ferrous salts in solutions such as Azcona and Martin pointed out [4]. This can be explained on the grounds that the transformation of material into the vapor phase in our case took place from the liquid phase, while in their case this occurred from the solid form (precipitates on needle electrodes) where the diffusion processes were bound to affect the results.

We did not find any data in the literature on the question of third element effects in the analysis of melts involving the use of sparks. It is known, however, that if a powerful excitation source is employed, e.g., a Volbank arc, then third element effects are far less pronounced. Sukhenko [16] has shown in this case that the metal is molten to a greater depth. In this case, therefore, we have two diffusion coefficients to deal with: a) the coefficient in the molten metal which is independent of third element effects; and b) a diffusion coefficient in the adjacent part of the solid. It is natural, therefore, that when the amount of molten metal increases as the result of using a more powerful spark, third element effects will decrease.

3. It is known that if one works with a low power spark [17], then the analytical results depend on the structure of the test material. This is easily explained by means of the hypothesis developed, since the diffusion coefficient depends on the structure of the crystalline lattice.

4. The effect of changes in the amount of test element on the line intensity of the base element can be observed in a number of instances. E.g., V. K. Prokofiev [18] pointed out that during the analysis of zinc in bronze, the slope (i.e., the tangent of the angle between the straight-line graph and the horizontal) of the graph is equal to ca. 4 (for an ignition time of ca. 1 minute). We ourselves, during analysis of CaO in slags, the slag being in tablet form, got graphs whose slopes were 2.4. This contradicts the generally accepted hypothesis according to which the slope of the graph is equal to the reabsorption coefficient, which cannot be greater than one. Prokofiev [18] explains the increase in slope by an increase in zinc concentration cutting down the amount of copper changed into vapor. In this case Lomakin's formula should be written as follows:

$$\frac{I}{I_0} = \frac{ac^{b_1}}{c^{b_2}}, \qquad (4)$$

where c is the concentration of test element; b_1 is a factor which characterizes reabsorption, b_2 is a factor which characterizes the effect of test element concentration on the amount of base element changed into the vapor phase. This explanation can be physically based on the hypothesis we have developed, since the diffusion coefficient of copper can change with changes in concentration of test element. In confirmation of this position we can advance facts which derive from the physics of solid bodies. Thus, Gruzin, Korneev, and Kurdyumov [21], found that the self-diffusion coefficient of γ-iron depends to a significant extent on carbon content. For a carbon content of 4.5% (atomic), ϵ is approximately halved as compared with pure iron, while the value of D_0 under these conditions decreases more than 10 times.

5. Usually the effect of a third element increases as its concentration increases; sometimes, however, a saturation phenomenon appears, when a further increase in third element concentration beyond a certain concentration shows no further effect on the analysis.

This is clearly demonstrated in Table 1, borrowed from Azcona and Martin's work [4]. Gertsriken and Dekhter [5], observed similar phenomena during a study of third element effects on the diffusion coefficient. They showed that the rate of diffusion of mercury in lead depends on the amount of magnesium, and does not depend on changes in the amount of antimony. Addition of 0.41% Sb lowers the

diffusion coefficient of mercury, but further addition of Sb within the limits 0.41 - 1.6% has no effect. Thus, the saturation of the third element effect, which has been observed in certain cases during spectrochemical analysis, can be explained, together with similar phenomena, by means of the diffusion coefficient.

TABLE 1

Concentration of Sn in relation to Zn (atomic)	Displacement of graph Pb/Zn	Concentration of Pb in relation to Zn (atomic)	Displacement of graph Sn/Zn
4	0.117	6	0.306
5	0.185	8	0.435
6	0.240	10	0.664
7	0.243	12	0.663
8	0.259	-	-
9	0.266	-	-

6. Instances are known where the extent of the third element effect depends on the nature of the upper electrode and the way in which it is ground. This problem has been studied in detail by Vorontsov [19]. The facts adduced in his article can hardly be explained by oxidation-reduction processes on the electrode. E.g., it is incomprehensible why, on switching over from one type of electrode to another, the sign of the effect of Sn on Pb/Cu should be reversed. It is also not clear why, when an aluminum electrode with a diameter of 0.5 mm is used, the effect of Sn on Pb/Cu is greater than when the aluminum electrode has a diameter of 5 mm, though on Filimonov's hypothesis the reverse should be the case, since grinding an electrode to an area with a smaller diameter is equivalent to increasing the sparking time, which should according to Filimonov's theory, lead to a decrease in the third element effect. Here again it is necessary to resort to the diffusion theory in order to explain these phenomena. A decrease in the diameter of the upper electrode leads to a smaller sparking area, i.e., to a concentration of energy in a smaller volume, and to a corresponding increase in temperature of the metal layer under the oxidized surface. A change in the material of the upper electrode, as I.M. Veselovskaya, V.G. Koritsky, and L.N. Filimonov have shown, also leads to a change in the sparking area, and consequently affects the temperature of these parts where the diffusion processes develop actively. It follows from equations (3) and (4) that the diffusion coefficient depends not only on the activation energy and entropy energy, but also on temperature. As a result, the relative amounts of test and reference elements which diffuse to the surface for equal amounts of third element will depend essentially on the temperature of the metal adjacent to the sparking area. A change in this temperature arising from a change in the material and shape of the cathode will affect third element effects.

7. Of considerable interest is the work of Koritsky and Edneral [20], who have shown that, starting at a certain limiting size, heating of the sample takes place, which leads to very significant changes in analytical results. E.g., in one of the experiments where the sample, which weighed 2.5 g, was thermally insulated, ΔS for Mn/Fe was +0.300, while for the same sample, non-insulated $\Delta S = -0.120$. It is interesting that ΔS for the reducing agents Mn, Si, and Cr increases with decreasing sample size. From the views developed by Veselovsky, Koritsky, and Filimonov on the basis of selective oxidation, it follows that for slow oxidation rates the relative intensity of the reducing agents Cr/Fe, Si/Fe, Al/Fe, should increase. This is confirmed by experiments in which the upper electrode needle is substituted by a metallic one. In the case given above where small samples are used, they are initially heated up, and consequently there is an increase in oxidation, but despite this the relative intensity of the reducing agent increases and does not decrease as would be expected on Filimonov's theory. Here again, the diffusion theory has to be called in to explain these changes in the relative intensity of the lines with changes in sample weight; according to this theory, the relative amounts of test material and base material which diffuse to the surface vary with changing temperature. At the same time, of course, selective oxidation processes also come into operation, and one of these phenomena apparently masks

the other, and to distinguish between them is extremely difficult sometimes.

8. Twyman, Zenden, and Dreblaw, while developing a method for analyzing cadmium in copper [22], found one sample which would simply not fall on the graph; chemical analysis gave a value of 0.92% Cd for the sample, while spectrochemical analysis indicated a Cd content of >1.0%. The sample was cast from the same materials as the other standards. The authors carefully studied this sample; it was analyzed several times in various laboratories; contaminants were determined, its micro-structure, hardness, and thermal conductivity were all studied, and it was subjected to the same thermal treatment as other standards; the sample was cut and sparked at different spots, and in every case the spectral analysis gave higher results than chemical analysis. The authors could not find the reason for this difference. Only after dissolving the test sample did spectrochemical analysis give values of 0.92-0.94% Cd, which is in good agreement with chemical analysis. The authors gave no explanation for this phenomenon. We think that the reason for the anomalous behavior of this sample is that the presence of third elements leads to changes in the diffusion coefficients. True, the authors did not find any third elements in this sample in amounts greater than in any of the other standards; from the physics of solid boides, however, it is known [23] that diffusion coefficients depend not only on the amount of third elements, but also on their disposition; if the third element should be segregated along the grain boundaries, then the change in the diffusion coefficient which results will not correspond to its average content in the sample. We think that the only possible explanation of the anomalous behavior of this sample is that the contamination (third elements) is segregated on the grain boundaries and leads to a considerable change in the diffusion coefficients which do not correspond to the content of third elements in the test sample[1]). When the test sample is brought into solution, the crystalline structure is broken, and all its defects in the way of segregation along the grain boundaries also disappear, so that no further anomalous behavior occurs. We have gone into some detail on this particular sample because spectroscopists often come across samples which give different results according to whether the analysis is carried out spectrochemically or chemically. Usually no explanation can be advanced for these divergencies. Here, apparently, we must turn our attention not only to the amount of third elements, but also to their possible segregation along the grain boundaries. It would be desirable to study all such samples by bringing them into solution.

9. Prokofiev [18], during a study of the calcining curves of Silumin, found that a layer of thickness 0.05 mm is formed on the metal surface, which differs appreciably from the base material of the electrode in hardness. At the same time, oxidation processes come into operation on the electrode surfaces; the analysis of oxidized grains, however, showed that there is no appreciable difference between the composition of the metal and the oxides. Thus, changes in the relative intensities of the lines during calcining cannot be explained in this case by selective oxidation. Prokofiev only connects this change in relative intensities with the appearance of characteristic "tempered" layers. However, in the discussion of Prokofiev's article [18], S. I. Fishman poses a natural question: how can one explain the effect of structure on the line intensities of Si, if, according to Prokofiev's hypothesis, evaporation of metal occurs from "little pools" of molten metal where the structures are of course not neutral, and whether the "pools" are formed from metal tempered by sparking or from untempered metal. To explain this phenomenon it is only necessary to ascribe an important part to diffusion processes. In the initial stages of sparking, the pools are formed directly from the electrode metal. Subsequently, during the sparking process, an intermediate layer is formed between the original metal and the pools, and naturally the diffusion velocity through this layer may differ essentially from the diffusion velocity in the base metal. Accordingly, the film surface from which transformation of the material into the vapor phase occurs will differ in chemical composition from the original material, although on the whole the composition of the oxidized layer does not differ from the composition of the original material.

1) Naturally, ordinary metallographic analysis cannot detect this segregation.

10. It is interesting to compare the conditions which hold during the transformation of a material into the vapor phase during spectral analysis with the mechanism of cathodic atomization. According to Gippel's [24] theory which has been developed in detail recently by Taunes [24], the energy of the impacting ion during cathodic polarization is transferred to several metal atoms, and in this way a very small part of the atomized surface is heated. As a result of thermal conductivity, the temperature of the heated part falls rapidly, subsequently some evaporation occurs which is the reason for cathodic atomization. The quantitative results obtained by Taunes are in good agreement with the experimental results for high gas pressure and a small cathodic drop. The main difference from cathodic atomization in the case of a condensed spark is that a very large amount of energy is localized on small areas; this leads to explosive evaporation (jets are thrown out). Explosive evaporation is the result, apparently, of the fact that under suitably chosen discharge conditions, temperatures are developed which are higher than the boiling point of the elements which make up the sparked surface. In this way it is possible to explain the fact that during a spark discharge there is no fractional evaporation which is so characteristic of arc discharge, where the temperature of the molten parts is usually lower than the boiling point of the surface components.

During cathodic atomization, localization of considerably less energy occurs than when a condensed spark is used; this leads to fractional evaporation. In the latter case the metal surface is only comparatively slightly heated, and therefore during cathodic atomization no active diffusion processes which occur near the surface subjected to the action of a condensed spark, develop. By means of these two factors — fractional evaporation and the absence of diffusion — it is also possible to explain the fact that during cathodic atomization considerable changes in the composition of the atomized surface can be observed in many instances. E.g., an alloy of silver and copper which in external appearance does not differ very much from silver, after prolonged atomization acquires the appearance of copper, since the silver is atomized far more rapidly than copper. Addition of 10% magnesium to the silver almost completely stops atomization of silver [24]. As far as we know similar phenomena have not been observed during the action of a condensed spark on a metal surface. Thus, the difference between cathodic atomization and transformation of a material into the vapor phase during a spark discharge is determined first of all by the amount of localized energy. This quantitative difference, in the case of a condensed spark gives rise to a qualitatively new phenomenon — diffusion in the surface layer and explosive evaporation which eliminates fractionation.

Unfortunately, a quantitative check on the diffusion theory which we have developed is extremely difficult. First, it is very difficult to separate oxidation-reduction from diffusion processes. It is also exceedingly difficult to evaluate the temperature in those layers where diffusion is active. In addition, in contrast to purely diffusion experiments, we have to deal with a temperature gradient and not with constant temperature. This complicates matters further. Finally, one has to bear in mind that high temperatures in the layers adjacent to the spark area lead to structural changes in the test material which are difficult to assess.

The value of any theory in the final count is determined by the practical conclusions which can be drawn from it. We think that the following practical conclusions may be derived by uniting the diffusion theory with Filimonov's selective oxidation theory.

In order to nullify third element effects it is essential that: a) the transformation of a material into the vapor phase should take place from a liquid phase in conjunction with spark excitation; b) the test sample should

be either completely oxidized or should contain an excess of strong reducing agent which does not participate in the analysis, so that no oxides of the test elements should appear on the surface of the melt. The simplest method of achieving these requirements is by working with aqueous solutions, when the transformation into vapor phase occurs directly from the liquid phase. The use of aqueous solutions, however, is only a half measure, since under such conditions undesirable effects connected with dissolution of the test sample come into play. The following more simple and general method of analysis may be put foward: briquettes are made from powder or filings; these are melted at high frequency from a separate generator, and maintained in this state during exposure time; excitation is by a controlled spark. In order to eliminate selective oxidation effects, the test material is either completely oxidized with a stream of oxygen (just as for example steel turnings are oxidized during carbon determinations), or on the other hand completely reduced by addition of strong reducing agents which do not participate in the analysis. One can use as standards in this case the same samples (as turnings or powder) as are used for chemical analysis, mixed in any proportions.

It must be borne in mind that in developing this new method of spectrochemical analysis, one is bound to come up against considerable technical difficulties. While there is about 20 years experience behind spectral analysis of solid samples, as far as we know, spectral analysis of alloys in conjunction with spark technique has not been applied anywhere, and there has been no research in this field.

SUMMARY

1. On the basis of a large amount of experimental material published in papers on spectral analysis on the one hand, and in papers on the physics of solid bodies on the other, a theory is postulated which takes into account the role of diffusion in processes occuring on electrodes, which lead to third element effects during spectral analysis involving the use of spark excitation.

The practical conclusions of this theory are; in order to eliminate third element effects, it is essential to break down the crystal lattice, i.e. to transform the test material to a liquid state and to use spark excitation. At the same time the sample should be completely reduced or completely oxidized, so that no oxidation-reduction processes can occur in the surface (according to Filimonov's theory).

2. It is essential to organize experimental work in order to develop new methods of spectral analysis on the basis of this theory.

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Observations during Correction. 1. In a recent issue of the journal Spectrochimica Acta (V, No.6, 507, 1953) there is a short reference to a report of Frederickson and Churchill, who connect errors in the spectrochemical analysis of aluminium with the "metallurgical history" of the sample, and they consider that in order to increase the accuracy of the analysis it is essential to work with molten test material in conjunction with spark excitation. The authors tested various methods of melting test materials with this aim in view and on the basis of their preliminary results came to the conclusion that the most convenient method of melting is induction heating; thus, the authors of this paper, like ourselves, reckon that in order to increase analytical accuracy it is essential to break down the crystal lattice, since with the breakdown of the structure, it is natural that all the changes in the electrodes which are related to the "metallurgical history" of the sample also disappear. The authors, in contrast to us, do not give any

explanation for the mechanism of the effect of changes in the state of the electrode on the result of spectral analysis. On the other hand, we only suggested the expediency of using induction heating for melting the test for spectrochemical analysis, while they have demonstrated this possibility experimentally with aluminium.

2. Of interest is the work of T.T. Magel, P.A. Kulip, and A.R. Kauffman [Problems of Contemporary Metallurgy, No.4, p.143, (1953) and J. Metals, 4 (12), 1286-1288 (1952)] in which are described carefully worked out methods of induction heating of metals which do not involve the use of crucibles. By using this method for melting the test electrode it should be possible to use a stream of flowing metal for analysis; in this case oxidation-reduction processes on the electrodes will not have any significance.

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THE THEORY OF ANALYTICALLY-ACTIVE GROUPS

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Saratov State University

Fairly recently one of us advanced the hypothesis [1], that in addition to the functional analytical groups which are present in a molecule of an organic reagent, and which determine the mechanism of the analytical reaction, there are other groups of atoms which, while not essentially affecting the reaction mechanism, nevertheless affect the character of the end product of the reaction, and thereby exert a considerable effect on the sensitivity. Such atomic groups were called analytically-active groups. The introduction of an analytically-active group into an organic compound which is capable of undergoing certain reactions converts the compound into an analytical reagent.

According to Kuznetsov [2], when a colorless organic reagent reacts with an ion to give a colored reaction product, the chromophoric action of this ion is displayed. In the case where the interaction of a colored reagent with an ion leads to the formation of a changed, more intense, and usually deeper color, the auxochrome action of the ion is manifested, as shown by one of us previously [3]. This latter effect is determined by the effect of the metal ion on the intramolecular ionic state of the reagent molecule.

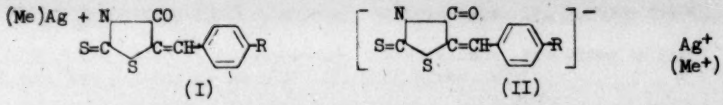
If one considers the colored compounds formed by reaction of an organic reagent with an inorganic ion from the point of view of Dilte and Vitsinger's theory it is possible to come to the following conclusion, as Kuznetsov [4,8], and Kulberg [5], did independently of each other; the greater the polarity of the reaction product, other conditions being equal, the more intense the color. Usually the reaction sensitivity increases in parallel with increasing color intensity of the reaction product. Consequently, if such a molecule contains a positive or negative auxochrome, then the introduction into the molecule of another suitable auxochrome or anti-auxochromic groups, which leads to an increase in the polarity of the compounds, increases the intensity and depth of its color and consequently increases the sensitivity of the reaction.

If one considers that the metal plays the part of an auxochrome then the introduction, into a compound capable of reacting, of another suitable auxochrome (i.e., one of similar sign- anti- or pro-auxochromic) leads to the effect indicated above. The correctness of this hypothesis was shown by Kuznetsov [6,8], during a study of the effect of substituents in the molecules of certain azo dyes and other compounds on the colors of the products of their reaction with Ti (IV) and other elements.

The capacity of rhodanine and its derivatives to serve as analytical reagents for a number of ions is well known [14] In acid media this group of compounds reacts with Cu^{I}, Ag^{I}, Hg_2^{II}, Hg^{II}, Au^{III}, Pd^{II}, Pt^{IV}, Os^{VIII}.

The reaction mechanism is not the same in all cases: for Ag^{I}, Cu^{I}, Hg^{II}, Hg_2^{II}, - salt formation; for the others in all probability, complex formation.

One of the following formulas can be ascribed to the silver salt of rhodanine and its derivatives:

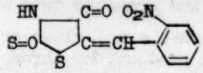


(I) (II)

The difference between these two formulas is that in (I) the rhodanine compound of the metal is regarded as an intramolecular ionic compound, in a state of intramolecular dissociation [7], while (II) is purely ionic.

In the case considered, Formula II has a low probability, because it presumes that the color of the compound is the same (in solution), apart from the nature of the Me, which is not confirmed by experiment.

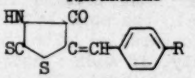
Formula I corresponds to an intraionic state, and consequently the color of the corresponding compounds will be deeper and more intense the greater the difference in polarity of both parts of the molecule. This effect will be manifest to a stronger degree when an auxochrome is found in one part of the molecule, and an anti-auxochrome in the other. Since with increasing positive character, R increases (see Discussion of Results) the color intensity of the respective substituted benzylidenerhodanine, it is possible to postulate that the anti-auxochromic effect is concentrated in the rhodanine part of the molecule. As proof it may be pointed out that the compound



and its silver salt, which contain an anti-auxochrome in the benzylidene residue [8], do not differ in color in acid or alkaline media from benzylidene, but, like it, have a pale yellow color.

TABLE 1

Color and Values of the Molar Extinction Coefficient of Benzylidene-Substituted Rhodanine



R	Color of a 0.03% acetic solution of the reagent	ϵM at λ_{max}
H	Rosy brown	$2.0 \cdot 10$
OCH_3	Lemon yellow	$1.5 \cdot 10^3$
OH	Lemon yellow	$3.3 \cdot 10^3$
$N(CH_3)_2$	Orange-yellow	$4.1 \cdot 10^4$
$N(C_2H_5)_2$	Orange	$6.4 \cdot 10^4$

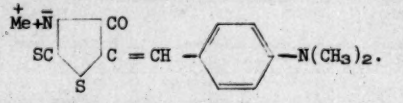
The colors and molecular extinction coefficients of benzylidene derivatives of rhodanine containing different substituents in the benzene ring are compared in Table 1. It is clear from the table that an increase in molecular extinction coefficient is parallel with increases in the positive character of the auxochromes, which can be arranged in the following series, in order of increasing activity [9]:

$$H < OCH_3 < OH < NH_2 < N(CH_3)_2 < N(C_2H_5)_2.$$

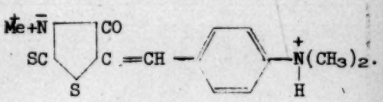
An extremely important fact is that the character of the colors of the compounds adduced in Table 1 changes only to a comparatively small extent with introduction of the respective substituents. In order to find a reason for this it is necessary to examine the rhodanine part of the molecule; we can establish the presence of two anti-auxochromes >C=O and >C=S, and two pro-auxochromes >NH and S, which are located in the heterocyclic ring. It is known [9], that when an auxochrome and an anti-auxochrome are present in the same molecule, they mutually compensate each other.

Since the imino group in rhodanine and its derivatives is subject simultaneously to the ionic action of two anti-auxochromic groups, then its hydrogen will be replaceable by a metal; when this occurs compounds are formed which are considerably more deeply colored than the original reagents. Obviously,

as a result of substitution of hydrogen by metal the total negative character of the rhodanine part of the molecule increases. This phenomenon is probably related to the increasing heteropolar character of the bond on going from >NH to >NMe, which is also favored by the polarizing interaction between metal and reagent. A more detailed explanation of this phenomenon may be found in the theory of intramolecular dissociation [7]. As a result of intramolecular dissociation the metal communicates a negative character to one of the parts of the reagent molecule, which also gives rise to electrical polarity with positive substituents of the type $-N(CH_3)_2$, located in the second part of the molecule:



In accordance with theory, in acid media the color of the compound formed between metal and rhodanine compounds is deeper, since in this case the electrical polarity of both parts of the molecule increases:



The aim of the present article is an experimental study of the question under consideration, and also to explain the effect of the non-rhodanine part of the molecule (of analytically-active groups) on the sensitivity of the interaction between the class of compounds indicated and a number of metal ions.

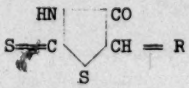
EXPERIMENTAL

I. Syntheses of Rhodanine Derivatives

In all, 17 rhodanine derivatives were examined; of these benzylidene rhodanine [10], p-diethylaminobenzylidene rhodanine [11], p-dimethylaminobenzylidene rhodanine [12], o-hydroxybenzylidene rhodanine [10]; m-hydroxybenzylidene rhodanine, p-hydroxybenzylidene rhodanine [10], o-hydroxynapthalene rhodanine [10], p-methoxybenzylidene rhodanine [13], and furfurylidene rhodanine [10], were prepared according to published methods. 5-Bis(p-diethylaminophenyl)-methylene rhodanine and 5-bis-(p-dimethylaminophenyl)-vinylene rhodanine were kindly given to us by G.M. Oksengendler. The remaining 6 compounds were prepared for the first time[1].

All the new rhodanine derivatives were prepared by condensation of the respective aldehyde with rhodanine in an aqueous medium in the presence of sodium acetate, sometimes in the presence of piperidine. They were all identified by their sulfur and nitrogen contents and by means of their molecular weights.

Table 2 contains details of some of the characteristics of the new compounds of type



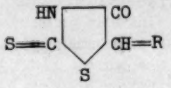
II. Discussion of Results

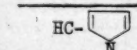
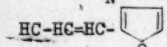
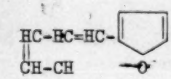
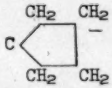
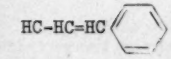
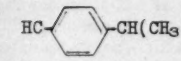
1. The Effect of the Nature of Substituents in the Benzene Ring on the Sensitivity of Reactions with Substituted Benzylidene Rhodanines. According to the hypothesis developed above the sensitivity of the respective reactions should be increased by successive introduction of auxochromes of increasing

[1] P.S. Dichkova and M.N. Zavalishina both students participated in the syntheses of these compounds.

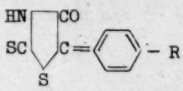
TABLE 2

Analytical Results Characterizing some Rhodanine Derivatives of the Type



R	Formula	Melting point (°C)	N content		S content		Molecular weight	
			Calc.	Found	Calc.	Found	Calc.	Found
	$C_8H_6ON_2S_2$ ..	228-230	13.33	13.58	30.50	30.00	210.2	209.4
	$C_{10}H_7O_2NS_2$..	205	5.90	6.25	27.08	27.03	237.2	236.8
	$C_{12}H_9O_2NS_2$..	200 (decomp.)	5.30	5.24	24.35	24.50	263.2	266.9
	$C_8H_9ONS_2$ ...	193	7.02	7.26	32.30	32.07	199.28	204.00
	$C_{12}H_9ONS_2$ ..	218-219	5.66	5.71	25.92	25.86	247.3	246.5
	$C_{13}H_{13}ONS_2$..	158-159	5.32	5.85	24.40	24.32	263.4	265.0

activity. Table 3 shows that the experimental results obtained are in good agreement with this hypothesis. If the total polarity of the reaction product formed between reagent and ion, other conditions being equal, determines reaction sensitivity, then on successive introduction into reagents of the general type

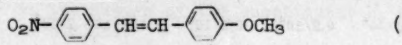


of group R with variable polarities, there will be a corresponding change in the polarity (total) of this molecule, and consequently in the senstitivity. To a first approximation the change in polarity may be evaluated from the value of the dipole moments of substituent R. Actually it is easy to see that the auxochrome series when arranged in order of increasing activity corresponds to a series of increasing dipole moments D for the respective groups in the aromatic nucleus [15]:

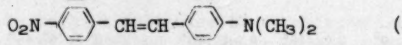
R	H	OCH_3	OH	$N(CH_3)_2$	$N(C_2H_5)_2$
D	0	1.25	1.49	1.58	> 1.70

It is obvious that the introduction of a group into the benzylidene rhodanine molecule should increase the electrical polarity of the two parts of the molecule, which leads to an increase in the dipole moment of the reagent molecule. The increase in molar extinction coefficient of the substituted benzylidene rhodanine, as shown clearly in Table 1, is a proof of this.

Published results [16], also confirm this point of view. Thus for the compounds:



(I)



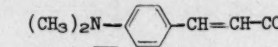
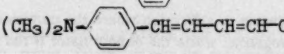
(II)

the dipole moments are respectively 7.8 D (I) and 8.3 D (II), while the dipole moments of the methoxy-and dimethylamino-groups are 1.25 and 1.48 D, respectively.

If the metal substituting the hydrogen of the imino group in a rhodanine derivative alters the state of the reagent molecule to one of intramolecular dissociation, then it is obvious that the greater the dipole moment of the substituent R, the more deeply and intensely colored will be the silver or other suitable metallic derivative of benzylidene rhodanine containing this atomic group. This in turn should increase reaction sensitivity. The part played by an analytically-active group, therefore, may be considered to be increasing the dipole moment of the final analytical reaction product. Thus, in order to improve analytical reagents of the type considered, it is necessary to introduce into their molecules substituents which possess auxochromic activity (or anti-auxochromic activity) with the highest possible dipole moment. It should be noted that the iso-propyl group possesses the properties of a fairly strong auxochrome, approximating to that of the methoxy group (see Table 3).

2. The Effect of Conjugated Chain Length on Reaction Sensitivity.

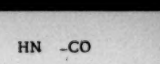
From dye chemistry it is known that the intensity and depth of dye color depends to a very large extent on the length of the conjugated chain joining the auxochromes [9]. This question has been studied in particular detail using cyanine dyes as examples [17]; in these dyes it has been shown that on increasing the number of vinylene groups, which are amphoteric auxochromes, deepening of color occurs. Published results also indicate an increase in dipole moment of the molecule with increasing number of vinylene groups, e.g. [16]:

	D
	5.3
	6.7

It would be natural to expect a similar effect in the case of rhodanine derivatives and an increase in the number of vinylene groups should be paralleled by increased sensitivity. Actually, as Table 3 shows, this effect is observed for all the ions studied during the application of polymethene derivatives of benzylidene and furfurylidene rhodanines as reagents. One can conclude, therefore, that an increase in conjugated chain length in reagents of the type considered is a factor which improves reagent properties, and may be recommended as a means of attaining this end. It follows, however, that one must take into account that in those cases where an increase in the number of vinylene groups leads to a sharp increase in the color of the reagent itself, the sensitivity of the reaction when using such a reagent

TABLE 3

Effect of the Nature of Substituent R on Reaction Sensitivity* with Substituted Rhodanines.



R	Metals							
	Ag^{I}	Pd^{II}	Au^{III}	Cu^{I}	Hg_2^{II}	Hg^{II}	Pt^{IV}	Os^{VIII}
	$2/10^3$	$0.5/4\cdot10^3$	$2/10^3$	$2/10^3$	$2/10^3$	$10/2\cdot10^3$	$10/2\cdot10^2$	Reduced
	$1/2\cdot10^3$	$0.2/10^4$	$2/10^3$	$2/10^3$	$20/10^2$	$20/10^2$	$10/2\cdot10^2$	$20/10^2$
	$0.1/2\cdot10^4$	$0.2/10^4$	$0.2/10^4$	$0.4/5\cdot10^4$	$2/10^3$	$2/10^3$	$10/2\cdot10^2$	$20/10^2$
	$0.02/10^5$	$0.02/10^5$	$0.1/2\cdot10^4$	$0.04/5\cdot10^4$	$0.04/5\cdot10^4$	$0.001/2\cdot10^6$	$0.1/2\cdot10^4$	$20/10^2$
	$0.002/10^6$	$0.002/10^6$	$0.02/10^5$	$0.01/2\cdot10^5$	$0.01/2\cdot10^5$	$0.0002/10^7$	$0.01/2\cdot10^5$	$2/10^3$
	$2/10^3$	$0.04/5\cdot10^4$	$0.4/5\cdot10^3$	$0.2/10^4$	$20/10^2$	$20/10^2$	$1/2\cdot10^3$	$2/10^3$
	$0.04/5\cdot10^4$	$0.02/10^5$	$0.2/10^4$	$0.4/5\cdot10^3$	$0.04/5\cdot10^3$	$0.2/10^4$	$0.1/2\cdot10^4$	$2/10^3$
	$0.1/2\cdot10^4$	$0.02/10^5$	$0.2/10^4$	$0.2/10^4$	$2/10^3$	$2/10^3$	$0.1/2\cdot10^4$	$2/10^3$
	$0.02/10^5$	$0.02/10^5$	$0.2/10^4$	$0.2/10^4$	$0.04/5\cdot10^4$	$0.2/10^4$	$1/2\cdot10^3$	$2/10^3$
	$20/10^2$	$0.2\cdot10^4$	$2/10^3$	$0.2/10^4$	$20/10^2$	$20/10^2$	$10/2\cdot10^2$	$20/10^2$
	$2/10^3$	$0.2/10^4$	$2/10^3$	$0.4/5\cdot10^3$	$2/10^3$	$2/10^3$	$10/2\cdot10^3$	$2/10^3$
	$0.0/2\cdot10^5$	$0.04/5\cdot10^4$	$0.1/2\cdot10^4$	$0.4/5\cdot10^3$	$0.2/10^4$	$0.04/5\cdot10^4$	$0.1/2\cdot10^4$	$20/10^2$

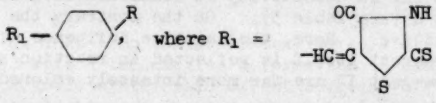
*Sensitivity is expressed as a fraction where the numerator is the limit of identification in micrograms, while the denominator is the reciprocal of the limiting dilution.

	$0.1/2\cdot10^4$	$0.02/10^5$	$0.1/2\cdot10^4$	$2/10^3$	$0.2/10^4$	$0.2/10^4$	$0.02/10^5$	$20/10^2$
	$4/5\cdot10^2$	$0.2/10^4$	$0.4/5\cdot10^3$	$0.4/5\cdot10^3$	$20/10^2$	$20/10^2$	$1/2\cdot10^3$	$20/10^2$
	$0.02/10^5$	$0.1/2\cdot10^4$	$0.2/10^4$	$0.2/10^4$	$2/10^3$	$0.2/10^4$	$1/2\cdot10^3$	$20/10^2$
	$0.01/2\cdot10^5$	$0.04/5\cdot10^4$	$0.2/10^4$	$0.04/5\cdot10^4$	$0.4/5\cdot10^3$	$0.4/5\cdot10^4$	$10/2\cdot10^2$	$20/10^2$
	$0.01/2\cdot10^5$	$0.02/10^5$	$0.1/2\cdot10^4$	$0.02/10^5$	$0.04/5\cdot10^4$	$0.04/5\cdot10^4$	$1/2\cdot10^3$	$2/10^3$

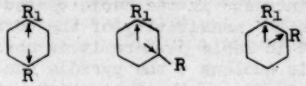
may not increase, but on the contrary decrease, as a result of the masking of the color of the reaction product by the reagent itself. This possibility is noted in the literature [8]. Such an instance is observed during a comparative evaluation of rhodanine reagents synthesized on the basis of Michler's ketone.

3. The Effect of the Position of the Substituent in the Benzene Ring in Benzylidene Rhodanines on Reaction Sensitivity. The values of the dipole moment of reagent molecule and of the reaction product corresponding to it depend not only on the nature of the substituent R, but also on its position in the aromatic nucleus.

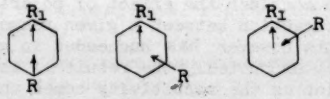
In considering the complex molecules of substituted rhodanines, particularly those containing so-called irregular atomic groups (i.e. those groups whose axis of momentum does not coincide with a line passing through the carbon atom of the benzene ring and the atom of the substituent groups linked to the carbon atom), it is very difficult to foresee exactly the effect of the position of substituent R on the value of the total dipole moment of the molecule. If one depicts the molecule of a substituted rhodanine as:



then to a first approximation one can envisage the following possibilities: where the moments of groups R and R_1 are of equal sign, then the dipole moment will be least when the groups are in the para position with respect to each other, and will increase from the meta- to the ortho-position

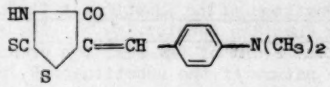


If the moments for groups R and R_1 have different signs, then the total moment of the molecule should diminish from the para compound through the meta to the ortho-position:



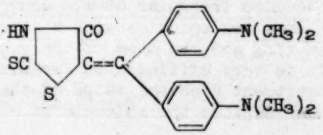
It is of course impossible to expect that this regularity will be manifested in a pure form since a multitude of other factors, in particular polarizing factors, will affect the total dipole moment. A study from this point of view of para-, meta-, and ortho hydroxybenzylidene rhodanine, as shown in Table 3, showed that in almost all cases the reaction sensitivity falls from the ortho- to the para-hydroxybenzylidene rhodanines. Since the negative end of the dipole falls on the hydroxyl group linked to the aromatic nucleus, then in accordance with what has been said above one can postulate that the rhodanine residue has the same sign for the dipole moment. One can expect also that in the case of amino- and amino-alkyl derivatives, where these groups are the positive ends of the dipole, it will be the para derivative which has the greatest sensitivity and the ortho derivative the least.

4. The Effect of an Additional Auxochrome. It is known from color theory that intra ionic compounds with two auxochromes located in the same part of the molecule are more deeply and intensely colored than compounds with only one auxochrome. In accordance with this, the silver salts of compound I



I

are less deeply colored than the salts of compound II



II

Nevertheless, as far as sensitivity is concerned, reagent II has no advantage over reagent I (see Table 3). On the contrary, the latter is sometimes even more sensitive. Here, the negative influence of the characteristic color of the reagent itself is reflected in reaction sensitivity, since solutions of reagent II are far more intensely colored than those of reagent I.

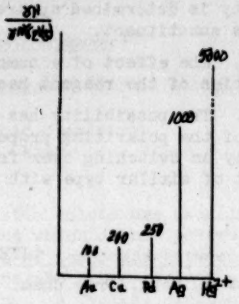
5. Effect of the Nature of the Ring Connected to the Rhodanines on Reaction Sensitivity. It is natural to assume that not only the nature of the substituent, but the nature of the ring itself to which the substituent is linked, should have an essential effect on reaction sensitivity. One should expect that with an increase in the basic character of the nucleus there will be an increase in the sensitivity of the corresponding reagent. This is clearly demonstrated in Table 3, where it is obvious that it is the compounds with the most basic nucleus – the pyrrole nucleus – which have the greatest sensitivity. As far as the derivatives of benzene, pentacyclomethylene, and furane are concerned, their sensitivities are for the most part very similar to one another.

6. Effect of the Metal Used on Reaction Sensitivity. Several attempts have been made to consider the effect of polarizing factors on the sensitivity of the interaction between a given reagent and a given ion [3]. None of these attempts however has succeeded in giving sufficiently definite results. This is undoubtedly the result of the fact that such a characteristic of a reaction as the sensitivity comes under the influence of a multitude of additional factors, which are not taken into account when the question is dealt with from the purely polarization point of view.

Among these factors we can include, e.g., the nature of the bond between ion and reagent, the nature of the reaction product, the kinetic characteristics of the reagent, steric hindrance, etc.

If as a basic value one should take not the absolute sensitivity of a given reagent, but the change which occurs on going from a reagent with the minimum polarity to an exactly similar reagent but with the highest possible polarity, then this value will be a direct function of the change in polarity of the reagent; while all the other factors will be evened out since they remain more or less constant for a given group of reagents. Let us try to forecast from this viewpoint the nature of the changes in sensitivity for elements reacting with rhodanine derivatives in a weakly acid medium. In

considering the results for Pd^{II}, Au^{III}, Cu^{I}, Ag^{I}, Hg^{II} (Os^{VIII}, Pt^{IV}, and Hg_2^{II} are excluded from consideration, since the mechanism of the reactions for the first two elements are still unexplained, while for Hg_2^{II} the character of its polarization interaction is not clear), one can first of all assume that changes in sensitivity should be less for Pd^{II} and Au^{III} than for Ag^{I}, Cu^{I}, Hg^{II}. This is obvious from the fact that the first 2 ions with valency states of II and III have an electronic structure comprising 16 electrons, and it is well known that the polarization action of ions with an incomplete shell is less than one with an 18 electron shell.



Change in reaction sensitivity of ions of certain metals on switching from benzylidene rhodanine to p-diethyl aminobenzylidene rhodanine.

For all group II ions from the group considered, a strong polarizing capacity is combined with a tendency to deformation. Since within the same group of the periodic system this effect increases from top to bottom, then it should be displayed to a greater extent in Ag^{I} than in Cu^{I}. Comparing, in their turn, Ag^{I} and Hg^{II}, which have equivalent outer electronic shells and values for the ionic radius which are almost equal, we can forecast that the doubly-charged mercury ion should have a greater polarizing effect than the singly-charged silver ion, since the polarizing effect of an ion increases rapidly with increasing charge. On the basis of all that has been said above, the following order can be postulated for the changes brought about by changes in the polarizing properties of the ion:

$$\left.\begin{matrix} Pd^{II} \\ Au^{III} \end{matrix}\right\} < Cu^{I} < Ag^{I} < Hg^{II}.$$

It is clear from Fig.1, where the ratios of limits of identification for benzylidene- and p-diethylaminobenzylidene- rhodanine are plotted along the ordinate, that the experimental results are in complete agreement with the hypothesis advanced.

It must be emphasized once more that comparing the polarizing action of ions is only possible when considering compounds of the same type; the greater the difference in polarity between extreme cases of the type considered the more clearly expressed will be this regularity.

SUMMARY

On the basis of a study of the reaction sensitivity of 17 rhodanine derivatives (6 of which were synthesized for the first time) with 8 ions, it has been established that:

1. The part played by an analytically active group in a given case is increasing the polarity (dipole moment) of the molecule formed as the result of reaction between reagent and ion.

2. An increase in the number of vinylene groups in a reagent molecule as a rule leads to an increase in sensitivity as a result of increasing polarity of the molecule.

3. The effect of the position of a substituent R on reaction sensitivity is determined apparently by the direction of the dipole moment of this substituent.

4. The effect of a number of structural factors on the analytical properties of the reagent has been studied.

5. The possibility has been demonstrated of forecasting (on the basis of the polarizing properties of an ion) changes in reaction sensitivity on switching over from a reagent with a low polarity to a reagent of similar type with a greater polarity.

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THE USE OF COLORED REAGENTS IN COLORIMETRY[1)]

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Reagents which possess their own characteristic colors are usually used for the colorimetric determination of cations which do not possess chromophoric activity [1]. During the formation of compounds between such a reagent and metallic cations a shift of the absorption spectrum is observed or a new, more intense band is formed. A typical example of the use of such a reagent is the determination of aluminium by means of alizarin, aluminon, etc.

The use of colored reagents in colorimetry gives rise to a number of difficulties [2]. One of these difficulties is a result of the fact that such reagents usually have indicator properties, and therefore a change in color may be evoked not only by the formation of a colored complex with the metal to be determined, but also by a change in pH of the solution. If, however, the pH is carefully controlled, this effect can be eliminated.

Of greater complexity are questions connected with the characteristic color of the reagent itself. The color of excess reagent is superimposed on the color of the complex formed, as a result of which the straight line relation between optical density of the solution and the concentration of the test element is destroyed. Determination by colorimetric methods thereby becomes impossible, or necessitates corrections for the characteristic reagent color, which naturally lowers the accuracy [3, 5].

When colored reagents are used in colorimetry the most convenient method to adopt is the scale method [2]. Nevertheless, even in this case the characteristic color of excess reagent decreases the sensitivity of a determination. Thus, for low aluminium concentrations it is difficult to observe the weak rose color of aluminium alizarate on the background of the yellow color of excess alizarin. When calibration curves are used the curve does not pass through the origin, and the lift in the curve at the beginning (i.e. at low concentrations of aluminium) is very small.

In the present work we have studied one of the methods of eliminating the optical difficulties mentioned above. For the colorimetric determination of aluminum by means of alizarin, we used a method of extracting the excess reagent; by this method the influence of the color of excess alizarin on the color of the aluminum alizarate solution is eliminated. Aluminum alizarate is not extracted with non-aqueous solvents.

This method can be applied to stable compounds. As a proof that aluminum alizarate is not decomposed during extraction of excess alizarin with ether, it has been shown that during 2-3 extractions of excess alizarin with ether, the third extraction is not colored yellow by alizarin.

Both alizarin and its sodium sulfonate (alizarin S) were used as reagents for aluminum determination. Alizarin S dissolves readily in water and is only poorly extracted by non-aqueous solvents. Alizarin

(unsulfonated), although it is only slightly soluble in water, is easily extracted from aqueous solutions with ether. Alizarin was therefore used in the method employed for eliminating the effect of excess colored reagent.

During colorimetric determination of aluminum by means of alizarin, the pH has to be strictly controlled. Strict control of the pH of the aqueous phase over a definite range during extraction of excess alizarin is also essential. On increasing the pH >5.5-6 the alizarin in the aqueous phase passes over into an intensely colored ionic form (the unisubstituted sodium salt is formed). In this form alizarin is not extracted with organic solvents. Nevertheless, at a pH of 5-5.5 for the aqueous phase – the one usually used for the determination of aluminum – extraction of excess alizarin permits the sensitivity of the determination to be increased considerably; moreover, a straight line relation is observed between aluminum concentration and solution color.

The optical characteristics adduced below were obtained by means of an FM photometer. Maximal light absorption by aluminum alizarate is observed in the 496-533 mμ region of the spectrum. For a light filter with an effective wave length of $\lambda = 496$ mμ the molar absorption coefficient of aluminum alizarate (AlAliz) is equal to[1] $\epsilon_{AlAliz} = 1.7 \cdot 10^4$. In this part of the spectrum the molar absorption coefficient of the reagent amounts to $\epsilon_{H_2Aliz} = 10^3$.

During colorimetric determination, a known amount of alizarin is added to the test solution independently of the amount of aluminum present, since this is not known. At appreciable concentrations of aluminum the alizarate color will be readily observable. Thus, if the amount of aluminum amounts to 1/10 of the amount of reagent added, then the optical density (D_{AlAliz}) which is determined by the aluminum alizarate will be found to depend on the optical density (D_{H_2Aliz}) determined by the residue of alizarate as follows:

$$\frac{D_{AlAliz}}{D_{H_2Aliz}} = \frac{0.1 \cdot \epsilon_{AlAliz}}{0.9 \cdot \epsilon_{H_2Aliz}} = \frac{0.1 \cdot 1.7 \cdot 10^4}{0.9 \cdot 10^3} \approx 1.7$$

However, at low concentrations, e.g., for a ratio of Al: H_2Aliz = 1:100, the reaction has a low sensitivity; in this case the ratio of optical densities determined by alizarate and alizarin, respectively, will be as follows:

$$\frac{D_{AlAliz}}{D_{H_2Aliz}} = \frac{1 \cdot \epsilon_{AlAliz}}{100 \cdot \epsilon_{H_2Aliz}} = \frac{1 \cdot 1.7 \cdot 10^4}{100 \cdot 10^3} = 0.17$$

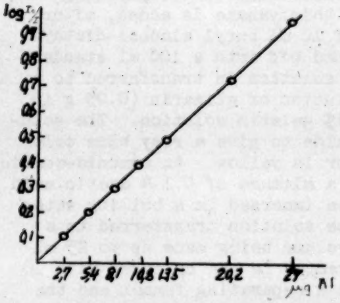
i.e., the optical density of the solution, determined by aluminum alizarate, amounts in all to only 0.17 of the optical density determined by the excess of colored reagent (alizarin). It will be difficult, therefore, to observe the color of the aluminum alizarate. On extracting excess alizarin with ether, this masking effect is removed. Apart from the increase in sensitivity

1) The results obtained are approximate since aluminum alizarate is insoluble in water; the light absorption of colloidal solutions using gelatin as the stabilizer was measured.

2) Alizarin S was used for these measurements, since alizarin is only very slightly soluble in water and its saturated solution is colorless.

which is observed when excess alizarin is extracted with ether, a straight line relation holds between optical density of the aluminum alizarate solution and aluminum concentration; moreover, the straight line of optical density – aluminum concentration passes through the origin.

The graph shows the calibration curve for a light filter with a transmission region at 496 mμ. Optical density is plotted along the ordinate and aluminum concentration in micrograms in 15 ml solution (aqueous phase) along the abscissa.



Excess alizarin was removed by extraction. Various organic solvents were tried for the extraction. Best results were obtained with ether. Alcoholic solutions of alizarin were used. Aluminum alizarate is formed more rapidly on heating the solution. For further work, therefore, the solutions were heated on a water bath.

The optical density of aluminum alizarate solution was measured without excess alizarin. A consideration of the graph shows that a straight line relation holds between optical density of the solutions and their aluminum content over a range of 2-25 μg aluminum in 15 ml solution. The solutions of aluminum alizarate were stable with time. Identical results were obtained when color intensity was measured immediately, and 24 hours after the formation of the alizarate.

Colorimetric Determination of Small Amounts of Aluminum in Metallic Zinc

The presence of small amounts of aluminum (of the order of tenths or hundredths of a per cent) in metallic zinc is of great importance in hot galvanizing. For best quality coating, aluminum in amounts up to 0.3% is added to the galvanizing bath. Of published methods of determining aluminum in the presence of large amounts of zinc, N. I. Lekhovitsky's work [4] should be mentioned; he proposed a method for determining aluminum in zinc alloys containing up to 4% aluminum. His method is based on the removal of zinc by hydrolysis, precipitation of aluminum as aluminum hydroxide with ammonia, and subsequent determination of aluminum as phosphate. This method is suitable for zinc alloys containing relatively large amounts of aluminum, but it requires a lot of time.

We have worked out a method for the colorimetric determination of aluminum in zinc which is based on the formation of aluminum alizarate. The optical density of aluminum alizarate solutions in the absence of zinc and in the presence of zinc in amounts of 0.1 - 0.2 g/10 ml was the same. Zinc, therefore, in amounts of 0.1 - 0.2 g/10 ml does not interefere with the colorimetric determination of aluminum.

Iron is one of the worst elements for interfering with the colorimetric determination of aluminum as alizarate. Iron forms a brightly colored lac with alizarin. Iron was removed by extracting it in the form of an iron thiocyanate complex with a mixture of butyl alcohol and ether in the ratio of 2:5. The use of this mixture permits iron to be removed in amounts of 10-15 mg from 25-40 ml of test solution on using two to three extractions. The possibility of separating aluminum and iron was checked on synthetic mixtures. The results obtained are adduced in Table 1.

TABLE 1

Al taken in μg	Fe added in mg	Al found in μg	Deviation μg
40	10	45	+ 5
50	10	45	- 5
60	20	60	0
70	20	70	0
75	30	70	- 5
85	40	80	- 5

These results show that aluminum and iron can be separated from each other satisfactorily by this method.

The following procedure was adopted for the determination of aluminum in metallic zinc:

0.1 - 0.2 g of zinc is dissolved in 5 ml of sulfuric acid (1:10), after which $KMnO_4$ solution is added to oxidize iron; a small excess of $KMnO_4$ does not interfere, since it is subsequently decolorized by treating with thiocyanate. The solution is transferred to a separating funnel, 5 ml of 4 M solution of ammonium or potassium thiocyanate is added, after which the iron is extracted with three lots of 10 ml butyl alcohol-diethyl ether mixture (5:2). The water phase is drained off into a 100 ml standard flask and diluted to the mark. 10 ml of this solution is transferred to a test tube, 0.5 ml of a saturated alcoholic solution of alizarin (0.03 g in 100 ml alcohol) is added, followed by 2 ml of 1% gelatin solution. The solution is made alkaline with 0.5 N sodium hydroxide to give a rosy blue color when 0.1 N acetic acid is added until the color is yellow. An ammonia-acetic acid buffer of pH 5 is added to the solution (a mixture of 0.1 N acetic acid + 0.1 N NH_4OH in the ratio of 3:2) and the tube immersed in a boiling water bath for 5 minutes. The tube is cooled and the solution transferred to a cylinder for colorimetric determination, the volume being made up to 25 ml with buffer solution. Excess alizarin is extracted in the cylinder with 10 ml ether. The ether layer can be separated in a separating funnel and the color intensity of the aqueous phase measured in a photometer or colorimeter. The color intensity of the aqueous layer is compared with the color intensity of the aqueous layers of standard solutions of aluminum alizarate prepared in the same way. Several standard solutions of aluminum alizarate should be prepared containing varying amounts of aluminum. The method suggested was checked by the method of addition to synthetic mixtures containing 0.1 - 0.3 g zinc. The results obtained are adduced in Table 2.

TABLE 2

Zn taken in g	Al added in mg	% Al in the Zn	Fe added in g	Al found in mg	% Al
0.2	0.08	0.040	0.002	0.075	0.038
0.1	0.06	0.060	0.002	0.06	0.060
0.2	0.05	0.025	0.002	0.05	0.025
0.2	0.07	0.035	0.02	0.07	0.035
0.2	0.1	0.050	0.02	0.105	0.052
0.2	0.1	0.050	0.002	0.11	0.055

These results show that the method proposed is completely satisfactory. Aluminum can be determined by this method in one hour.

SUMMARY

1. For the determination of aluminum with alizarin a new colorimetric method involving the use of colored reagents is employed; this includes extraction of excess reagent with a non-aqueous solvent and subsequent colorimetric determination of the complex compound in the aqueous phase.

2. A method is proposed for the determination of small amounts of aluminum in metallic zinc based on the formation of aluminum alizarate.

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THE QUANTITATIVE DETERMINATION OF OPIANIC ACID

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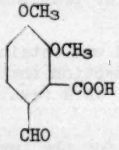
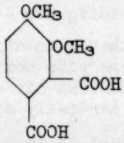
Opianic acid has recently begun to find wide use in the pharmaceutical industry for the preparation of medicinal preparations. This necessitates working out a method for its quantitative determination which is suitable for both pure opianic acid and for technical opianic acid, which also contains hemipinic acid.



Opianic acid



Hemipinic acid

Since alkalimetric titration is not suitable for the determination of technical opianic acid, we started looking for other methods, in particular for methods characteristic of the aldehyde groups present in opianic acid.

The work was carried out with opianic acid purified by two conversions through the pseudo ester The melting point of the product was 148-148.5° (published data 145, 150° [1]).

The percentage purity of the acid as determined by titration was 99.69 (more correctly, back titration). The usual methods used for the determination of compounds containing the carbonyl group, such as the sulfite and bisulfite methods and the formation of oximes, despite their application under the most diverse conditions, did not give positive results. Low and variable results were also obtained when opianic acid was determined by the formation of its anil derivative [2] - 81.94, 84.61%.

Much more consistent and higher results were obtained when methods based on the formation of various hydrazines of this acid were used. Thus, when phenylopiazone [3] – $(CH_3O)_2C_6H_2\begin{matrix}CH=N\\ |\\ CO-N-C_6H_5\end{matrix}$ – was prepared, the yield corresponded to 95% opianic acid. Even better results (97%) were given by the opiazone, $(CH_3O)_2C_6H_2\begin{matrix}CH=N\\ |\\ CO-NH\end{matrix}$ [4], which was prepared by heating opianic acid (3 parts) in concentrated aqueous solution with hydrazine sulfate (2 parts) and sodium acetate (3 parts), also in concentrated aqueous solution, for 30 minutes. This reaction seemed a promising one for the quantitative determination of opianic acid.

Actually, by changing the ratios of the components on the basis of a number of tests, so that the amount of hydrazine sulfate was 3 parts and sodium acetate 4 parts while the amount of opianic acid was left unchanged, and at the same time extending the heating period to 2 hours, we increased the yield of opianic acid to 98.0 – 98.5%.

The opiazone prepared, which was dried at 110°[1] melted (without recrystallization) at 164 – 166° (published results 166° [4]. We have not yet succeeded in raising the yield to 100% under the conditions employed. Nevertheless, when we took a synthetic mixture (60:40) of pure opianic acid and pure hemipinic acid (melting point of hemipinic acid, 170 – 170.5°; published results 175 – 179° and 177 – 178° [5]) and determined the opianic acid in it by the method described, we got mean values of 99.82%, (98.67, 100.8, 100.0%). The opiazone thus prepared melted at 164 – 165°, 165 – 166°, which indicates the absence of any contamination.

In order to check up on whether or not during the reaction hydrazides of hemipinic acid precipitate (if they are formed under these conditions), even though only partially, or hemipinic acid itself precipitates, we made some tests on the action of hydrazine sulfate and sodium acetate on pure hemipinic acid under the conditions employed above.

After 2 hours heating, no precipitate separated. No precipitate separated out even on standing for 48 hours.

The fact that a quantitative yield of opianic acid was obtained from its synthetic mixture with hemipinic acid leads to the assumption that hemipinic acid exerts a salting out effect on the opiazone which, as a result of a certain solubility, is partially soluble.

On this basis it is clear that this is the reason for the low results obtained when analyzing pure opianic acid.

In order to check this hypothesis, we used sodium chloride for salting out the opiazone from pure opianic acid solution instead of hemipinic acid. The amount of sodium chloride used was 10% of the opianic acid. The yield was raised to 99.5%. The melting point of the opiazone was 166 – 167°; i.e., it corresponds to the melting point of the pure opiazone. Numerous repeats of this reaction (with pure opianic acid and sodium chloride) confirmed the preliminary results obtained and gave good agreement in replicate determinations. Thus, for the same sample of opianic acid, we got 99.37, 99.48, 99.20, and 99.37%.

TABLE 1

Analysis of Pure Opianic Acid

Weight of opianic acid in g	Weight of NaCl in g	Weight of opiazone obtained in g	% of opianic acid	Melting point of opiazone in °C
0.3032	0.0360	0.2956	99.37	166-167
0.3041	0.0347	0.2968	99.48	
0.3021	0.0338	0.2940	99.20	166-166.5
0.3028	0.0333	0.2952	99.37	

Determination of opianic acid by means of opiazone is eminently suitable for the analysis of technical opianic acid. The opianic acid is determined from the opiazone (with addition of sodium chloride). Hemipinic acid is determined as follows: by titration with 0.1 N alkali total acids in terms of hemipinic acid are determined. From this total, the amount of opianic acid in terms of hemipinic acid is substracted, the difference gives the hemipinic acid content (Table 2).

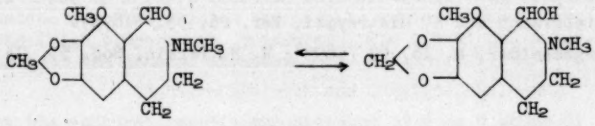
[1]) All the melting points given for the opiazone are for material dried at 110°.

TABLE 2

Analysis of Technical Opianic Acid

Number of sample	% Opianic acid, as determined from opiazone	Hemipinic acid content, in %	Loss on drying, in %	Chlorides, in %	Materials soluble in ether, in %	Total	Melting points of opiazone dried at 100°
1	54.82	41.38	3.51	None	None	99.71	163.5-165
2	97.92	1.27	None	None	0.26	99.45	165 -166
3	90.47	1.12	8.68	None	None	100.27	165 -166
4	51.25	43.2	3.50	Trace	None	97.95	164 -165

Since technical opianic acid, if incompletely washed from mother liquor, my contain traces of cotarnine which has an aldehyde group,



we carried out some tests on its interaction with hydrazine sulfate and sodium acetate under the same conditions as those used for the preparation of opiazone. No precipitate was formed, so that any possible contamination of opianic acid with cotarnine should not affect the results of opianic acid determinations.

Experimental Procedure for the Determination of Opianic Acid

About 0.3 g (accurately weighed) of opianic acid is weighed into a 100 ml conical flask, 0.03 g of pure sodium chloride is added and dissolved in 4 ml of water, and the mixture is boiled. At the same time a mixture of 0.3 g hydrazine sulfate and 0.4 g of anhydrous sodium acetate is dissolved in 2 ml of water by boiling in a test tube. The two boiling solutions are combined, the salt solution being added to the opianic acid solution. If on doing this, the solution becomes turbid, it is heated until the precipitate dissolves, when it is placed in a boiling water bath under a reflux condenser and heated for 2 hours. At the end of this period crystals of opiazone form, the amount of which increases considerably on cooling. After 4-5 hours, the opiazone is sucked dry on a No. 3 filter crucible; it is washed with small amounts of water (4-5 lots of 2 ml each) until the filtrate is free from sulfate and chloride ions (test with barium chloride and silver nitrate respectively).

The opiazone is dried to constant weight at 105-110°. The percentage of opianic acid is calculated from the formula:

$$\frac{a \cdot 1.0193 \cdot 100}{b} = \% \text{ opianic acid},$$

where a is the weight of opiazone obtained, 1.0193 is the conversion factor for opiazone ⟶ opianic acid, b is the weight of opianic acid taken.[1]

[1]) When technical opianic acid is being analyzed, there is no need to add sodium chloride.

SUMMARY

A method is described for the quantitative determination of opianic acid which is based on the formation of opiazone by the action of hydrazine sulfate and anhydrous sodium acetate.

This method can be used for the determination of both pure and technical grade opianic acid.

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ANALYTICAL METHODS FOR SIMPLE HALO-ETHERS

ANALYSIS OF α,β-DIHALO AND α,β,β-TRIHALOALKYL ETHERS

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The analysis of poly-halo derivatives of organic compounds has attracted the attention of many chemists [1, 2], and presents considerable difficulties. It is known [1], that an accumulation of halogen atoms in molecules of organic compounds leads to a sharp decrease in their reactivity as a result of which determination of total halogen can only be achieved under particularly stringent conditions (high temperature, pressure). The α,β-di and α,β,β-trihaloethylalkylethers of the general structure

$$CH_2Hal—CHHal—OR \text{ and } CHHal_2—CHHal—OR,$$

tested by the authors, despite the presence of 2 or 3 atoms of halogen, are exceptionally reactive [3,4]. Till recently only compounds of the general formula indicated above with R = C_2H_5 [5,6], were known. Subsequently, when simple vinyl ethers became generally available [7], a general method [3,4] was worked out on their basis for the synthesis of α,β-dihaloethylalkyl ethers:

$$CH_2=CH—OR + Hal_2 \rightarrow CH_2Hal—CHHal—OR.$$

α,β,β-trihaloethylalkyl ethers are formed as by-products of this reaction. In these test compounds, just as in mono halo ethers [8], the halogen atom which is in the α-position with respect to the alkoxy group can be readily substituted by other atoms and groups. In most cases the reactions occur at room temperature. The halogen atoms in the β-position remain untouched during the reactions. This characteristic behavior of the halo ethers is explained by the strong influence of the oxygen atom which possesses unique properties [4].

Of particular interest is the reaction of α,β-dihaloethylalkyl ether with water:

$$CH_2Hal—CHHal—OR + H_2O \rightarrow CH_2Hal—CHO + ROH + HHal.$$

A halo substituted acetaldehyde, alcohol, and hydrogen halide are formed. The latter can be titrated with alkali or silver nitrate. The rate of hydrolysis of these compounds is of the order of those of ionic reactions, and the reaction has been used for the quantitative and qualitative detection of α,β-dihaloethylalkyl ethers. Similar properties are possessed by other halo derivatives of the ethers which contain one halogen atom on the carbon atom with an alkoxy group. Thus in α,β-dichloropropyalkyl ethers of the type

$$CH_3—CH_2Cl—CHCl—OR$$

a considerable tendency for substitution of the α-halogen atom is observed [9]. Obviously the hydrolysis reaction can also be used for the analysis of these compounds. In α,β,β-trihaloethylalkyl ethers (II) the α-halogen atom is also capable of being replaced by a hydroxyl group on reacting with water; this reaction is, however, rather slow. In order that all the hydrogen halide evolved may be determined, it is necessary to shake the trichloroether with water for 30-40 minutes. Adjacent halogen atoms slow down the reaction in this case.

α,β-Di and α,β,β-trihaloalkyl ethers show the following qualitative reactions:

1) with fuchsin sulfurous acid, they give a rose color which rapidly changes to the violet characteristic of aldehydes.

2) with 2,4-dinitrophenylhydrazine, they interact forming crystalline derivatives of the respective halo-aldehydes.

3) with silver nitrate, an immediate precipitate of silver chloride is formed.

4) with methyl orange, they give a bright red color.

We analyzed poly-halo ethers by titration of the hydrogen halide evolved with alkali or silver nitrate. The Volhard method was used for the silver nitrate titrations; it is, however, more convenient to use the Mohr method, after preliminary neutralization of the hydrogen halide with alkali. In this case the halogen can be determined on one aliquot by two methods, one method serving as a check on the other.

EXPERIMENTAL

Table 1 contains some of the constants for the materials analyzed.

TABLE 1

Constants of the Halo Ethers Analyzed

Formula of the ether	Boiling point/ mm in °C	n_D^{20}	d_{20}^4	MR_D found	MR_D calculated
$CH_2Cl—CHCl—OCH_3$	24.5-24.7/11	1.4480	1.2377	27.94	27.43
$CH_2Cl—CHCl—OC_2H_5$	42.5-43.5/12	1.4435	1 1879	32.71	32.04
$CH_2Cl—CHCl—OC_3H_7$-iso	34-34.5/9	1.4430	1.1235	37.07	36.49
$CH_2Cl—CHCl—OC_4H_9$	50/6	1.4473	1.1024	41.47	41.28
$CH_2Cl—CHCl—OC_5H_{11}$-iso	81/16	1.4450	1.0716	45.91	45.90
$CHCl_2—CHCl—OCH_3$	50.5/9	1.4722	1.4710	32.24	32.29
$CHCl_2—CHCl—OC_2H_5$	51-52/5	1.4630	1.3195	37.05	36.91
$CHCl_2—CHCl—OC_3H_7$-iso	63-64/11	1.4640	1.2861	41.10	41.55

Quantitative Determinations Were Made as Follows

To 20 ml of water contained in a 150-200 ml flask fitted with a ground glass stopper is rapidly added an aliquot of the test halo-ether (preferably in a thin walled ampoule). The contents of the flask are shaken (the ampoule breaks) and after several minutes (for dichloro ethers, 10-15 minutes; for trichloro ethers, 30-40 minutes), they are titrated with 0.1 N alkali, using methyl orange as indicator. The acid equivalent or the molecular weight of the ether is thereby determined. If the percentage active halogen is to be determined, then the contents are titrated with 0.1 N $AgNO_3$, in the presence of $KCrO_4$ as indicator (Mohr's method). Methyl orange does not interfere with the titration. Active halogen can also be determined by titration with $AgNO_3$ according to the Volhard method, but in this case there is no preliminary neutralization (indicator ferric alum) (Tables 2,3).

TABLE 2

Quantitative Determination of Halogen in α,β-Dichloro- and in α,β,β-Trichloroalkyl Ethers

Formula of ether	Content of active halogen (as determined by titration with silver nitrate)					Total halogen (as determined by a combustion method)		
	Weight taken, in g	Amount 0.1 N $AgNO_3$ used	Cl^- found, in %	Cl^- calc., in %	% determined	Cl, found, in %	Cl calc., in %	% determined
$CH_2Cl—CHCl—OCH_3$	0.1322	10.17	27.21	27.52	99.00	54.85	54.92	99.86
	0.1623	12.45	27.22		98.93	54.75		99.63
$CH_2Cl—CHCl—OC_2H_5$	0.0910	6.33	24.68	24.79	99.54	50.00	49.65	100.70
	0.1081	7.53	24.72		99.72	49.83		100.21
$CH_2Cl—CHCl—OC_3H_7$-iso	0.2049	13.42	22.30	22.40	99.56	45.46	45.16	100.52
	0.1117	7.05	22.60		100.72	45.08		99.82
$CH_2Cl—CHCl—OC_4H_9$[1]	0.06617	19.489	20.91	20.76	100.70	41.17	41.45	99.31
	0.02665	7.835	20.90		100.52	41.31		99.68
$CHCl_2—CHCl—OCH_3$	0.0741	4.55	21.77	21.70	100.21	64.94	65.10	99.74
	0.1031	6.25	21.53		99.19	64.80		99.54
$CHCl_2—CHCl—OC_2H_5$	0.1149	6.33	19.45	19.98	97.31	60.04	59.95	100.02
	0.3113	17.15	19.48		97.47	60.23		100.50

[1]) For this ether results of microdeterminations are given.

TABLE 3

Results of Titrating α,β-Dichloro and α,β,β-Trichloroalkyl Ethers with 0.1 N NaOH

Formula of ether	Weight taken, in g	0.1 N NaOH used, in ml	Molecular weight found	Molecular weight calculated	% determined
$CH_2Cl—CHCl—OCH_3$	0.1082	8.41	128.6	128.96	99.74
	0.1623	12.55	129.3		100.20
$CH_2Cl—CHCl—OC_2H_5$	0.0910	6.29	144.6	142.97	101.20
	0.1081	7.53	143.1		100.01
$CH_2Cl—CHCl—OC_3H_7$-iso	0.2049	12.90	158.8	156.99	101.20
	0.1117	7.18	155.3		98.86
$CH_2Cl—CHCl—OC_4H_9$	0.2100	11.97	175.4	171.07	102.50
	0.2048	11.52	175.6		102.60
$CH_2Cl—CHCl—OC_5H_{11}$-iso	0.3968	21.29	186.6	184.94	100.90
	0.2752	15.00	183.4		99.13
$CHCl_2—CHCl—OCH_3$	0.0741	4.66	159.0	163.41	97.29
	0.1031	6.40	160.8		98.37
$CHCl_2—CHCl—OC_3H_7$-iso	0.4710	25.38	185.6	191.44	97.28

SUMMARY

A method has been worked out for the quantitative and qualitative analysis of α,β-dichloro and α,β,β-trichloroethylalkyl ethers, based on titration of the hydrogen chloride formed on their hydrolysis. By means of this method, it is possible to determine the degree of purity or the concentration of the halo ethers, and also to determine the position of the halogen atoms so that their structure can be established.

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1) See Consultants Bureau Translation, page 81.
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CERTAIN ANALYTICAL PROPERTIES OF DI-β-NAPHTHYLTHIOCARBAZONE AND ITS SYNTHESIS

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Di-β-naphthylthiocarbazone, which is an analog of dithizone, was synthesized by the Soviet chemist, I. B. Suprunovich; he also studied the general properties of di-β-naphthylthiocarbazone [1].

A comparative study of the properties of di-β-naphthylthiocarbazone and dithizone is of interest both from the point of view of accumulating material characterizing the effect of substituents on the properties of the dithizone group, and for its practical application for the determination of small amounts of metals.

EXPERIMENTAL

Di-β-naphthylthiocarbazone was synthesized by Suprunovich's method [1]. There is one very important drawback with his method; viz., incomplete conversion of the intermediate product in the synthesis – naphthylthiocarbazic naphthylhydrazine – into thiocarbazide, and the partial decomposition of the latter. This drawback is connected with the difficulty of heating the product evenly over a short time. As a result, the di-β-naphthylthiocarbazone is contaminated and has to be recrystallized several times. In order to eliminate this difficulty, a number of experiments were carried out to modify the last stages of the synthesis. It was experimentally established how the intermediate product could be spontaneously converted into the naphthylthiocarbazide.

The following method was adopted: 5 g of naphthylhydrazine was finely ground and decomposed in a separating funnel with 4 N sodium hydroxide (50 ml) under an ether layer; the alkaline solution was extracted 2-3 times with ether, the extracts being collected in a flask. The calculated amount of carbon bisulfide was then added dropwise with stirring into the flask. The white precipitate of intermediate product which separated out was filtered off, washed twice with ether, dried between filter papers, and then finely ground. The powdered intermediate product was then distributed in a thin layer over a piece of glass and kept in a vacuum desiccator for a few days. Control of the conversion of the intermediate product into naphthylthiocarbazide was achieved by control of the melting point temperature. On reaching a melting point of 145°, the powder was treated with 5% potassium hydroxide in 96% ethyl alcohol. The red solution obtained was immediately poured into 1% sulfuric acid in which di-naphthylthiocarbazone was precipitated. The precipitate was filtered, washed first with water and then with alcohol, pressed between filter papers, and dried in a desiccator.

We studied a number of the analytical properties of di-β-naphthylcarbazone. Tests showed that the substitution of C_6H_5 (of dithizone) by $C_{10}H_7$ leads to essential changes in the properties of the reagent. First, the limit of identification is affected.

We determined the limits of identification for copper, zinc, and mercury using dithizone and di-β-naphthylthiocarbazone respectively. The tests were made as follows: A known volume of di-β-naphthylthiocarbazone or dithizone

solution in carbon tetrachloride was introduced into a micro test tube; the concentration used was 2 mg/100 ml.

A solution of the test metal salt was then added. The volume of metal salt solution was kept constant, while the concentration was varied. The test tubes were shaken for 60 seconds. Results are given in Table 1 (for copper), Table 2 (for zinc) and Table 3 (for mercury).

TABLE 1

γCu^{2+} in 0.05 ml	Volume of reagent, in ml	Color of CCl_4 layer		Limit of identification in γ	
		Di-β-naphthylthiocarbazone	Dithizone	Di-β-naphthylthiocarbazone	Dithizone
0.050	0.05	Violet	Yellow-red	–	–
0.040	0.05	Violet	Pale violet	–	0.040
0.030	0.05	Blue-violet	Green	–	–
0.020	0.05	Blue-violet	Green	–	–
0.015	0.05	Blue	Green	0.015	–
0.010	0.05	Green	Green	–	–

TABLE 2

γZn^{2+} in 0.05 ml	Volume of reagent in ml	Color of CCl_4 layer		Limit of identification in γ	
		Di-β-naphthylthiocarbazone	Dithizone	Di-β-naphthylthiocarbazone	Dithizone
0.025	0.025	Blue-violet	Light red	–	0.025
0.020	0.025	Blue-violet	Green	–	–
0.015	0.025	Blue	Green	–	–
0.010	0.025	Blue	Green	0.010	–
0.005	0.025	Green	Green	–	–

TABLE 3

γHg^{2+} in 0.05 ml	Volume of reagent in ml	Color of CCl_4 layer		Limit of identification in γ	
		Di-β-naphthylthiocarbazone	Dithizone	Di-β-naphthylthiocarbazone	Dithizone
0.25	0.025	Red	Orange	–	0.25
0.15	0.025	Purple	Green	–	–
0.10	0.025	Violet	Green	0.10	–
0.05	0.025	Blue	Green	–	–
0.04	0.025	Green	Green	–	–

In conclusion I should like to express my thanks for valuable advice and guidance to I. B. Suprunovich, Candidate of Chemical Sciences, the former director of this part of the work.

SUMMARY

1. The spontaneous conversion of the intermediate product in di-β-naphthylthiocarbazone synthesis to naphthylthiocarbazide has been established.

2. Limits of identification have been established for copper, zinc and mercury, using di-β-naphthylthiocarbazone as reagent. In all cases the limits of identification are greater than for dithizone.

3. The increased sensitivity of reactions with di-β-naphthylthiocarbazone as compared with those of dithizone indicates a higher stability of the inner complex salts of di-β-naphthylthiocarbazone than that of the inner complex salts of dithizone.

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A NEW QUALITATIVE REACTION FOR LIGNIN

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The reagents most often used for detection of lignin are certain phenols and nitrogen containing compounds [1-4]. Color reactions given by lignin with chlorine and sulfite, and with concentrated hydrogen halides are also used. Thus, lignin gives a green color when it reacts with concentrated hydrochloric acid. Other reactions have also been used for detecting lignin. We have previously [5] described a hydrogen sulfide reaction for lignin.

New observations have shown that lignin-containing materials also give a greenish color when tested with cupric nitrate. As in the previous work, papers of different types were used as test objects containing lignin (wrapping paper, low grade writing paper).

A normal solution of cupric nitrate is used. The reaction sensitivity was determined as follows: a 2 N solution of cupric nitrate gave an intense color with materials containing lignin (initially this solution was prepared for the determination of sulfur contents of certain organic materials). This solution was diluted twice and then its sensitivity checked again, until a solution was obtained which gave a just-observable but definite color with wrapping paper. The limiting concentration of cupric nitrate at which a color was still observable with lignin was 0.001 N.

A test is best carried out as follows: a 2 N solution of cupric nitrate is prepared (best results are obtained with a saturated solution). A few drops of test solution are placed on the material to be tested for lignin. Color should develop in a few minutes.

Different samples of wrapping paper treated in this way gave a yellow-green color. Similar results were obtained when text book paper, writing paper and newspaper were tried. It was observed during these tests that the poorer the quality of the paper, the more intense the green color obtained, and vice-versa. Lignin-free cellulose (hygroscopic cotton wool, and ashless filter papers of various types) under such conditions gives a blue color.

The advantages of the cupric nitrate reaction for lignin as compared with the hydrogen sulfide reaction described previously and other reactions for lignin mentioned above [1-4], is its simplicity, rapidity, and absence of such volatile poisonous materials as hydrogen sulfide, hydrogen chloride, etc.

The method described, just like the hydrogen sulfide method permits one to get a rough estimate of the amount of lignin and cellulose in test materials (according to the intensity of the spot).

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A MECHANICAL P-TRANSFORMER

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The possibility has been demonstrated in a number of papers recently of "rectifying" the characteristic curve of the photographic emulsion within a wide blackening range by means of the transformation

$$P = W + \frac{1}{\gamma}(S - W),$$

where – the blackening $S = \log i_0/i$; $W = \log (i_0/i - 1)$, and $\frac{1}{\gamma}$ is the parameter. It has also been shown that it is expedient to use the relation $P = p \log I - i_p$ when carrying out spectrographic [1, 2], and X-ray spectrographic [3, 4, 5] analyses. As shown experimentally, the transformation parameter $\frac{1}{\gamma}$ changes its value with different types of photographic film, and in general depends on the wave length of the light registered. This prevents the P-transformation from being universal, and necessitates calculation of the nature of the relation $P = P(S)$ for each actual value of the parameter.

In this paper we describe the construction of a mechanical set-up called the "P-transformer", by means of which the above calculations can be carried out automatically, thereby speeding up and simplifying their use. Of a number of possible variants of the transformer, we shall only consider the one which is most convenient to use. The schematic features of the P-transformer used in our laboratory are shown (Figure). It consists of a combination of a fixed semi-circular sector by means of which calculations of the value of $\frac{1}{\gamma}(S - W)$ are made graphically for various values of parameter $\frac{1}{\gamma}$, and of a movable straight edge which enables values of $\frac{1}{\gamma}(S - W)$ and W corresponding to different values of the blackening S to be added up.

The result of these calculations; viz., the value of $P = W + \frac{1}{\gamma}(S - W)$, is read off on the last scale of the transformer. The movable radius of the sector enables any value of $\frac{1}{\gamma}$ to be fixed in the interval −3 to +3. The latter values are disposed on the contour of the circular sector on a scale proportional to the cosine (the outer scale on the diagram) or the cotangent (the inner scale on the diagram) of the angle of inclination of the movable radius vector to the horizontal. In the first case (a) the universal (rectified for all values of $\frac{1}{\gamma}$) scale of the values of $S - W$ (corresponding to the values of S in the interval C to 2) should be arranged on the movable radius vector; in the second case (b) on the fixed ordinate axis. In both cases the abscissa of the point of intersection of the radius vector with the straight line parallel to the X axis, corresponding to the selected value of the blackening S, will be equal to $\frac{1}{\gamma}(S - W)$. If this point of the horizontal scale of the circular sector is made to coincide with point $W = 0$ of the nomogram $W = W(S)$ plotted on the movable straight edge,[1] then the result of calculations of P will be read off on the result scale at a point lying on one of the verticals from the point characterizing the blackening of the line on the movable straight edge. For this purpose a cursor, moving parallel to the horizontal axis and fitted with a fine vertical thread not shown on the diagram, is used.

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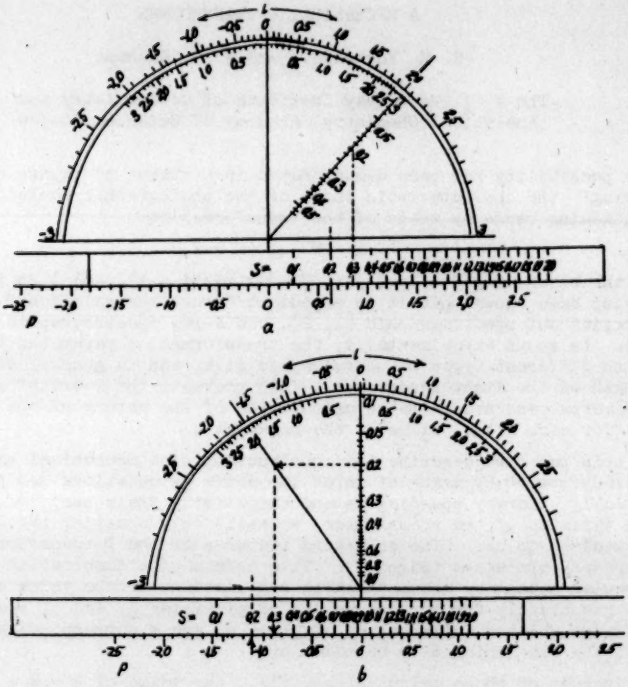
1) This point corresponds to a value of $S = 0.3$, and (Figure) is denoted by a two-way arrow.



The procedure for using the P-transformer for carrying out the calculations indicated above; e.g., for calculating P corresponding to S = 0.2 and $\underline{1}$ = + 2 is made clear from the diagram (case a and b) by the dotted lines and arrows.

In constructing one of these P-transformers, one must remember that the value of the diameter of the circular sector is of decisive importance; its value may be chosen arbitrarily, after which the scales of all the other parts are linked together, the actual values being determined by the limits of the variables. They are calculated by the usually accepted principles of nomography [6]. As shown experimentally, having chosen D = 200 mm, it is possible to construct a P-transformer by means of which it is possible to calculate values of P corresponding to various S values, and to carry out the reverse calculations in regions of low blackening with an accuracy of up to 0.01.

In those exceptional cases where such accuracy is insufficient, the use of a mechanical transformer will be of little good, since it would be very large.

In the majority of cases, however, the accuracy of 0.01 should be sufficient. The use of such a set-up,[1] particularly if it can be manufactured, should prove of great benefit to a large number of spectroscopists working either with the visible or X-ray part of the spectrum.

Received October 13, 1952.

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1) See Consultants Bureau Translation, page 403.
2) See Consultants Bureau Translation, page 385.
3) See Consultants Bureau Translation, page 347.

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1) We also tried out another variant of the transformer in which calculations were made of the values of $\frac{1}{}$ (S − W) on a logarithmic scale. The instrument is more compact. It was, however, not so convenient to work with as the one described above.

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DISCUSSION

A REPLY TO B. V. IOFFE'S ARTICLE, "THE ADDITIVITY OF REFRACTIVE DISPERSION AND A COMPARATIVE EVALUATION OF DISPERSOMETRIC METHODS OF DETERMINING AROMATIC HYDROCARBONS"[1])

B. A. Kazansky, M. I. Rozengart, O. D. Sterligov, and G. A. Tarasova

In the course of our present work we came up against the necessity of determining the aromatic hydrocarbon content of mixtures of hydrocarbons containing other hydrocarbons as well, in particular paraffin hydrocarbons, rapidly and in a small volume of test liquid. We tested a number of analytical methods and finally settled on methods involving the use of specific or relative dispersions. The work which we carried out during 1946-48 on checking the applicability for this purpose of the values of specific dispersion δ_{FC} (Grosse and Wackher [1]) and the relative dispersion ω_{FCD} (Mokhnatkin [2] and Ioffe [3]) showed that for a number of mixtures containing benzene and toluene, these values do not follow the additivity rule. Other authors [4], came to the same conclusion including Ioffe [5]. Accordingly, in his calculations based on relative dispersions, he had to introduce empirical coefficients, and then carried out his calculations by the method of successive approximations.

In 1949 Musaev [6] showed that it is possible to avoid introducing corrections if the benzene content is determined from the value of the difference between specific refractions of the mixture for two lines of the hydrogen spectrum.

In an article published in No. 5 of the J. Anal. Chem. for 1953 [7], we noted that it is possible to avoid introducing corrections in the determination of benzene and toluene in a number of mixtures by using the values of ω_R:

$$\omega_R = \left[\left(\frac{n_F^2 - 1}{n_F^2 + 2} - \frac{n_C^2 - 1}{n_C^2 + 2}\right) : (n_D - 1)\right] \cdot 10^3$$

It is easy to see from the results adduced in Table 4 of our article that for mixtures of hexane-benzene and heptane-benzene, particularly when the results are expressed graphically, the values of ω_{FCD} (relative dispersion calculated according to Ioffe's method) do not follow the additivity rule; at the same time the values of ω_R (calculated by means of the equation given in our article), characterizing the content of benzene in the mixture, follow this rule (Figs. 1 and 2). From the results given in Table 5 of our article, it follows that for mixtures of n-heptane-toluene, the values of ω_{FCD} do not follow the additivity rule; neither do the values of ω_R follow this rule for the mixtures enumerated above (Figs. 1 and 2), if toluene concentration is expressed in wt. %, but are additive if toluene concentration is expressed in molar % (Fig. 3). The values of ω_{FCD} and ω_R for mixtures of methylcyclohexane-toluene

[1]) See J. Anal. Chem., 9, 60 (1954).

also follow the additivity rule, if for calculating ω_{FCD} the toluene concentration is expressed in terms of weight %, and for calculation of ω_R, in molar % (Fig. 4).

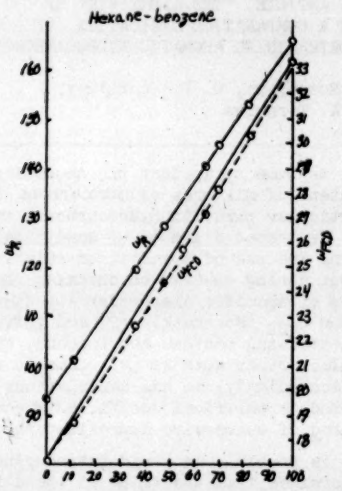

Fig. 1

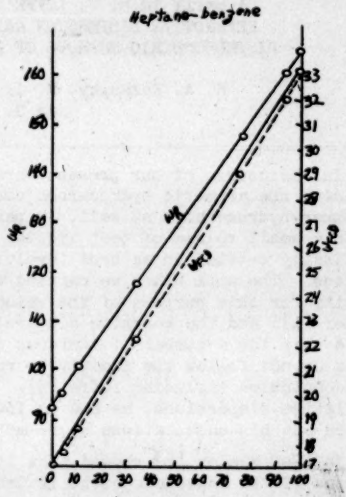

Fig. 2.

Our article led B. V. Ioffe [8] to protest that he fails to see any justification for our preference of ω_R to ω_{FCD} (or δ_{FC}) proposed by him, stating that "the expediency of introducing a new method should obviously be based on a careful comparison of both methods, using experimental results for the same test materials under identical conditions."

We never suggested that our formula should replace the equations relating specific and relative dispersions of hydrocarbon mixtures with their aromatic content. In so far as these equations embrace a large amount of experimental data, we were only concerned with results relating to 5 series of mixtures.

Neither did we regard the use of ω_R as a new method of determining aromatics in mixtures, nor even called it a "method."

We should like to observe, however, that the values of ω, δ, and ω_R were calculated on the basis of experimental results obtained on the same test materials and under identical conditions; i.e., we compared them just as Ioffe recommends. Such a comparison led us to the conclusions set out at the end of our paper.

With respect to the numerous examples which B. V. Ioffe adduced in order to show the non-applicability of ω_R values (Tables 2 and 3 in B. V. Ioffe's article), they do not satisfy us because they are mainly mixtures which do not contain benzene and toluene (Table 2).

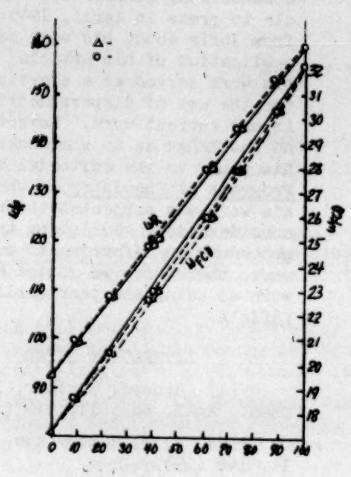

Fig. 3

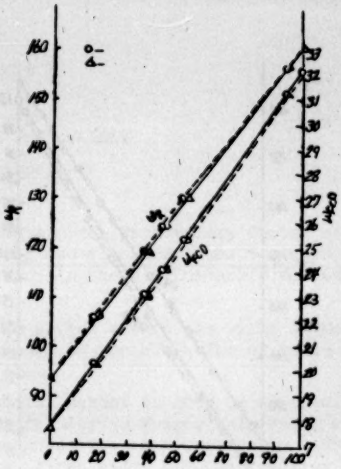

Fig. 4

B. V. Ioffe makes this further assertion: 'The very reliable results of G. S. Pavlov (for mixtures of benzene-cyclohexane. Authors.) do not confirm, rather they contradict the conclusion re the additivity of ω_R. The incorrect interpretation of these results by B. A. Kazansky et al is probably the result of errors in calculation." This assertion is based on a misunderstanding which can be explained by an inaccuracy in the text of our article. The additivity of ω_R values becomes apparent from G. S. Pavlov's results [9], when benzene concentration is expressed in molar %; under these conditions ω_{FCD} values display systematic deviations from additivity.

B. V. Ioffe reproaches us for not listing all his papers devoted to the application of dispersometry in hydrocarbon analysis, seeing in this apparently an attempt on our part to belittle his work. In our article we did not belittle the important contributions made by B. V. Ioffe on the study of refractive index, specific gravity, and dispersion of numerous individual hydrocarbons and also on the development of dispersometric methods of analysis. Nevertheless, since we had to consider the variants of these methods in a very condensed form, we did not consider it our task to draw up an exhaustive bibliography on the question. Accordingly in discussing B. V. Ioffe's work, we confined ourselves to a reference to one of his first articles (1946) and the latest (1950) known to us at the time of writing our paper, starting from which it is possible for the reader to find out all about B. V. Ioffe's work.

For the same reason we did not mention the possibilities of determining aromatic hydrocarbons by means of ω_{FC} values; this function is nothing new in principle and, in the words of the author, is an "improved variant of the method."

Finally, let us deal with B. V. Ioffe's assertion that we were wrong in dating his paper of 1946 a year later than that of Mokhnatkin's 1945, when in fact Ioffe reported on his work at the I.O.Kh.[1] of the USSR Acad. Sci.

[1]) I. O. Kh. = Institute of Organic Chemistry.

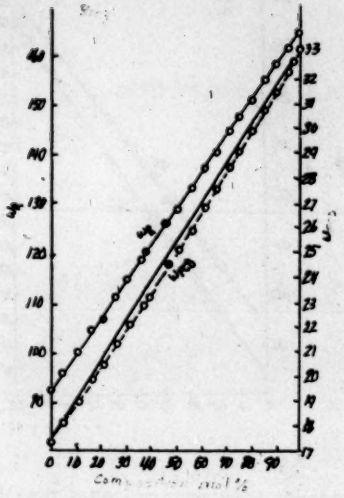

Fig. 5

considerably earlier and sent his article to press in April, 1945. We heard from Ioffe about his work before actual publication of his article. Moreover, his work served as a starting off point for the use of dispersometric methods in our current work. Nevertheless, we had no knowledge as to when Mokhnatkin sent his paper to the editorial board of Progress of Chemistry, or where and when his work was subjected to preliminary consideration. Following the customary procedure in referring to published work, therefore, we listed Mokhnatkin's work as being one year earlier than Ioffe's.

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[1]) See Consultants Bureau Translation, page 275.
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CHRONICLE

EVGENY STEPANOVICH PRZHEVALSKY

(On his 75th Birthday)

On the 12th of February, 1954 Evgeny Stepanovich Przhevalsky, Doctor of Chemical Sciences, celebrated his 75th birthday and also completed 50 years of scientific and teaching activity as a Professor in the M.V.Lomonosov Moscow State University.

During this half century Przhevalsky has worked within the walls of Moscow University, devoting all his energy and knowledge to the education of young chemists and instilling interest in science in them.

When he completed the Nezhinsky Classical School in 1898 he entered the Natural Sciences Section-Mathematico-Physics faculty in Moscow University, and ever since his scientific life has been connected with that University. While still a student, Przhevalsky started to work, first under V.V. Markovnikov and then under N.D. Zelinsky. In 1903 he finished his course at the University, graduating with first class honors. On completion of his degree he soon became an assistant in the Organic and Analytical Chemistry Faculty.

The history of the development of the school of analytical chemistry in Moscow University is closely linked with the name of Przhevalsky. In 1929 he took part in organizing a chair of Analytical Chemistry in the Chemistry Faculty of Moscow State University. In 1930 he was made head of this Chair.

The Analytical Section has always been his favorite. Being a first class teacher, he developed a corps of highly qualified analysts, who were mostly his own pupils. He built up the courses to a level capable of satisfying contemporary demands both on the scientific and pedagogic sides, and took an active part in drawing up the courses, theoretical and practical. On his initiative and under his direct leadership, a course of analysis of mineral raw materials, metals, and alloys was organized.

He did not confine all his research and teaching activities to the University, and after the October Revolution he took part in building up the Institute of Chemical Reagents. As an analytical chemist his specialty has been the determination of small amounts of contaminants in reagents. Przhevalsky has organized a large amount of work on the standardization of the quality of chemical reagents of Russian make. As a result of this work technical conditions of manufacture and methods of chemical testing for more than 200 reagents were confirmed by the Standardization Committee, and published subsequently in the form of a collection.

Przhevalsky has also done a lot of research on the determination of trace amounts, in the analytical section at the University, in conjunction with his students.

He has paid a lot of attention to organic reagents.

Przhevalsky has always been connected with the work of Institutes and factories; he has acted as a consultant for complex analyses requiring a lot of analytical experience and knowledge.

In addition to his scientific and teaching activity he has also edited a number of books and textbooks.

After organizing a Moscow branch of the Mendeleev Chemical Society he was

made chairman of the division, a position he held for many years.

From 1939-1944 Przhevalsky was Dean of the Chemistry Faculty. From 1939-1954 he has been head of the Scientific Research Institute of Chemistry in Moscow State University.

For his work he has been rewarded on more than one occasion. He has received the Order of Lenin and medals inscribed "For valorous work in the Great Patriotic War" and "Moscow- 800 years ".

We wish Przhevalsky many more years of fruitful work in the fields of teaching and science for the good of our Socialist country, and further successes in all his undertakings.

RESOLUTIONS PASSED BY THE ALL-UNION CONFERENCE ON THE APPLICATION OF M. S. TSVET'S CHROMATOGRAPHIC METHOD IN CHEMICAL ANALYSIS, CONVENED BY THE V. I. VERNADSKY INSTITUTE OF GEOCHEMISTRY AND ANALYTICAL CHEMISTRY AND IN WHICH THE COMMISSION ON CHROMATOGRAPHY OF THE DIVISION OF GENERAL CHEMISTRY OF THE ACADEMY OF SCIENCES, USSR, PARTICIPATED

(Moscow, November 18-21, 1953)

This conference, which was called to celebrate the 50th anniversary of the publication of M. S. Tsvet's first paper on chromatographic analysis, has shown that this new phenomenon discovered by the Russian scientist, M. S. Tsvet, has grown into a powerful instrument of analytical chemistry which permits the most difficult problems of practical and scientific interest to be solved.

At the conference, which was on a highly scientific level and in which the participants took an active part, more than 500 people from 39 cities attended the plenary sessions. Fifty-six reports were read and discussed. More than 70 people took part in the discussions.

The conference demonstrated the wide scope of scientific and applied research on chromatography in the Soviet Union and the attainment of the most important successes.

As demonstrated by the reports read at the conference, Soviet scientists are working on further developments in the theory of the chromatographic method of analysis (A. A. Zhukhovitsky); chemical hypotheses are being applied to existing physical views (D. I. Ryabchikov and V. I. Kuznetsov); new methods are being worked out for carrying out certain processes, complex chromatographic processes are being automatized (K. V. Chmutov); the scope of chromatography is being widened, and it is being applied in new fields. New methods, chromathermographic and thermodynamic, are being developed (A. A. Zhukhovitsky and N. M. Turkeltaub).

Russian research workers, having studied the materials used for chromatography from all angles, have decided, in particular, on a method for preparing silica gel with given properties (A. V. Kiselev and I. E. Neimark); new selective ion-exchange resins have been developed (V. A. Klyachko); methods of selecting the appropriate ion-exchange resin for a particular job have been worked out (D. I. Ryabchikov and coworkers, K. V. Chmutov, T. B. Gapon); some workers are concerned with the question of systematization.

Soviet scientists have perfected inorganic chromatographic analysis (F. M. Shemyakin, K. M. Olshanova, V. P. Meleshko, T. A. Belskaya and many others); analysis of biologically important organic compounds, including amino acids (T. S. Pakhina, E. N. Bezinger); carbohydrates (B. N. Zaitseva and M. S. Bardinskaya); intermediate products of photosynthesis (A. M. Kyzin, N. G. Doman); vitamins (B. G. Savinov); pigments and tannin materials (M. N. Zaprometov), etc.; analysis of other products, such as resins, cracking products (I. V. Kalechits, N. I. Medvedeva and others); gases (N. M. Turkeltaub); petroleum (S. D. Sergienko and others); pharmaceutical products (F. M. Shemyakin), and the analysis of many other materials.

The conference noted with satisfaction that the majority of the work carried out on chromatography by Soviet chemists was done with the Russian made ion-exchange resins. Recently the quality and variety of ion-exchange resins have improved. A large amount of work on the synthesis of ion-exchange resins and the ensuring of supplies to scientific establishments has been effected at the Mendeleev Institute Chem. Tech., Moscov (A. B. Davankov, I. P. Losev, E. B. Trostyanskaya). Work on the synthesis of ion-exchange resins has also been carried out at the I. V. S., Academy of Science, USSR (A. N. Vanshteidt, A. A. Vasilev and O. I. Orkhimenko) and in the State Institute of Planning, Chemical Engineering.

The Central Scientific Research Institute of the Cellulose and Paper Industry has worked out a method for manufacturing chromatographic paper.

The conference also stated that alongside these successes in the development of chromatography in the USSR, there are also a number of factors which hinder the wide application of chromatographic methods and their introduction in factory laboratories practice.

The Ministry of Chemical Industry has not hitherto issued a wide enough assortment of efficient ion-exchange materials synthesized by Soviet chemists, such as purified silica gel and activated charcoal, for laboratory and industrial needs. There are not enough special solvents and special reagents for chromatographic purposes, particularly for partition chromatography.

Special chromatographic paper has not yet been produced by the Ministry of the Wood and Paper Industry, while the experimental chromatographic paper prepared by the Central Scientific Research Institute of the Cellulose and Paper Industry still does not satisfy completely the requirements of analytical chromatographic paper.

The Ministry of Machine Construction has not produced special apparatus, including automatic apparatus, for chromatographic analysis.

Having considered the reports, the conference resolved as follows:

I. On the Further Development of the Theory of Chromatographic Analysis

That having considered a broad development of studies on theoretical questions to be essential, particular attention should be given:

1. To work out formulas by means of which analysts should be able to select optimal conditions for carrying out chromatographic experiments.

2. To formulate hypotheses enabling the analyst to direct chromatographic processes and to foresee the effect of various static and kinetic factors on these processes.

3. To work on the questions of physical and chemical theories of selective chromatographic processes.

4. To develop work on the study of the physical nature of sorption forces as the main causes of chromatographic adsorption processes, and to develop work on the study of diffusion processes.

5. In working on all these theoretical problems, together with explaining the physical essence of the process, it is also essential to clarify the chemical mechanisms of a given phenomenon.

In solving complex problems, one has to resort to complex methods of investigation with participation of analysts, physical chemists, physicists, etc.

II. On the Practical Application of Chromatographic Processes

1. To recommend further study of the automatization of chromatographic processes, and the construction of automatic set-ups and individual mechanisms.

2. To develop perfected apparatus, particularly for working under abnormal conditions, at different temperatures, in vacuum or under pressure, etc.

3. To carry out studies on the relation between sorption properties and sorbent structure, to develop direct methods for the quantitative and qualitative determination of functional groups in ion-exchange materials.

4. To carry out work on the search for selective chromatographic sorbents.

5. To develop work on the chromatographic separation of mixtures with components of similar properties, special attention to be given to the separation of fairly large amounts of material in good yield.

6. To intensify research on partition chromatography, which is of exceptional importance for the study of biochemical products (proteins, amino acids, carbohydrates, nucleic acids, hormones, vitamins, etc.). Particular attention to be given to the development of partition chromatography in the following fields:

a) to perfect methods for the qualitative determination and separation of individual groups of organic compounds;

b) to increase the sensitivity and accuracy of quantitative methods of determining various groups of organic compounds, separated on chromatograms;

c) to develop in conjunction with ion-exchange and adsorption chromatography a systematic scheme of analysis (by groups) of materials from plant and animal tissues;

d) to develop research in the field of partition chromatography of inorganic materials on paper, particularly for the analysis of small amounts of inorganic mixtures.

7. To intensify research on precipitation chromatography columns and on paper. To recommend the use of precipitation chromatography in conjunction with other techniques of chromatographic analysis for solving complex analytical problems.

8. To look for and to develop new fields for the application of chromatographic processes for the solution of questions of practical and theoretical analytical chemistry.

9. To widen the scope of research on chromatographic separation of elements at high dilutions, with the aim of concentrating them and for complete purification of the main component.

10. To intensify work on chromatographic preparation of small amounts of limitedly pure preparations of various substances of importance as standards.

11. To use chromatographic methods for the study of the properties of ions in solution, the study of the composition and the instability constants of complex compounds, and for other physico-chemical research.

12. To expand the application of chromatographic methods for the quantitative analysis of useful minerals, metals, alloys and other industrial products.

13. To use chromatographic methods for field work.

14. To study the secondary reactions of ion-exchange materials and their catalytic action.

15. To recommend the wide use of radiochemical and luminescence methods in chromatographic work.[1)]

III. On Organizational and Other Questions

1. To petition the Ministry of Machine Construction re the organization of the issue of standard types of special chromatographic apparatus, including automatic apparatus, ultrachemiscopes, chromathermographs, etc., and also set-ups for counter-current partition chromatography and densitometers.

2. To petition the Ministry of the Chemical Industry re the issue of enough of the sorbents used in chromatography, in particular:

- activated charcoal AG, AR, KAD, purified;
- silica gel, coarse and fine;
- chromatographic aluminum oxide;
- the cation-exchange resins KU-2, SDV-3, KB-4, RF, SBS;
- the anion-exchange resins MMG-1, PE-9, EDE-10, AN-2F, N-0.

It is also essential to increase supplies of the reagents used in chromatography - ninhydrin, orcine, 2,4-dinitrophenylhydrazine, bromophenol blue, bromothymol blue, bromocresol green, thymol blue, umbelliferone, and solvents for chromatography, particularly tertiary amyl and butyl alcohols, dioxane of mono methyl ether, ethylene glycol, and methylethylketone. To organize the issue of special flasks and plates of polythene.

3. To petition the Ministry of Chemical Industry to organize the distribution of chromatographic sorbents in small packages (1 kilo) and to sell them with other chemical reagents through Glavkhimreaktiv. Full details of the sorbent should be given with each package.

4. To petition the Ministry of Culture re the renewal of the issue of experimental lots of ion-exchange materials prepared at the High Polymer Laboratories of the Mendeleev Moscow Institute of Chemical Technology.

5. To ask the Ministry of Chemical Industry to establish a means of producing small amounts of experimental ion-exchange resins and membranes of polythene at the Frunze Scientific Research Institute of Plastics.

6. To petition the Ministry of the Wood and Paper Industry to produce better quality chromatographic paper than the experimental samples produced by the Central Scientific Research Institute of the Cellulose and Paper Industry. In order that paper of the right quality will be forthcoming it is essential:

To ask the Presidium of the USSR Academy of Sciences and the Ministry of the Wood and Paper Industry to petition together the Presidium of Ministers of the USSR and the Central Committee of the Russian Communist Party on the following points:

a) to authorize the Ministry of the Wood and Paper Industry to build during 1954-1955 a special factory for the production of all forms of analytical filter paper, including chromatographic paper, and to set up for this purpose a special, new paper-making machine.

1) The conference asks that authors should in the future give fuller details of the sorbents used. When working out methods of separating the elements, they should test the behavior of a greater number of elements and of more complex mixtures.

b) to engage the Ministry of Machine Construction to prepare and to supply the Ministry of the Wood and Paper Industry with paper-making machines for absorbent paper according to the current plan of the Scientific Research Institute of the Central Bureau of the Paper Industry.

c) to ask the Ministry of Industrial Products to supply the Ministry of the Wood and Paper Industry with 12 tons of new, white, cotton scrap in the first quarter of 1954 for the specific production of paper for chromatographic analysis.

7. To ask the Ministry of the Wood and Paper Industry to engage Leningrad Factory No. 2 to supply chromatographic paper until the special factory has been set up.

To ask the Ministry of the Wood and Paper Industry to include in the plans of the Central Scientific Research Institute of the Cellulose and Paper Industry, the development of the production of cellulose powder for chromatographic analysis and porous paper for spot tests.

8. To ask the Ministry of the Chemical Industry to organize the production of standard tubes of various sizes and construction for chromatographic analysis, and also other apparatus for supplying chromatographic set-ups (including special boxes and glass cuvettes for partition chromatography).

9. That all types of sorbents, chromatographic paper, and other materials used in chromatography be graded by the All-Union State Standard and Technical Specifications methods.

10. To petition the Commission on Terminology of the USSR Academy of Sciences to include in the Commission's plans the setting up of a rational scientific terminology for chromatography (processes, products, apparatus, etc.).

11. To ask the Ministry of Culture to introduce courses on chromatography in chemistry courses, including practical chromatography, and also include it in the courses of general or analytical chemistry given to students of biological, medical, geological, or other sciences.

12. To ask the Society for the Propagation of Political and Scientific Knowledge to organize a series of lectures on chromatography and issue popular pamphlets on the application of chromatography.

13. To organize a special course in chromatography at the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry.

14. To ask the Academy of SciencesPress to publish the work of M. S. Tsvet, including an introduction which reflects the present state of chromatographic methods.

15. To publish textbooks and practical handbooks on chromatography.

16. To organize an advisory board in conjunction with the Commission on Chromatography of the USSR Academy of Sciences.

17. To petition the Board of Scientific Films of the Ministry of Culture to make a scientific film of chromatographic analysis.

18. To ask the Presidium of the USSR Academy of Sciences to set up a memorial to M. S. Tsvet at Voronezh, in the house where he lived and worked.

19. To petition the Presidium of the USSR Academy of Sciences to establish an M. S. Tsvet prize, adjudged on the basis of the best work done every year in the field of chromatography.

20. To call regular conferences on the application of chromatographic methods in chemical analysis. The next to be called in 1956.

21. To ask the Commission on Chromatography to call a conference on the theory of chromatography in the first half of 1954.

22. To publish the papers presented at the present conference.

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ULTRA-MICRO CHEMICAL ANALYSIS

PART 3. POTENTIOMETRIC TITRATION

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GENERAL OBSERVATIONS

Until recently in carrying out volumetric determinations of a few micrograms of material one has had to work with rather dilute solutions, a method which is of course, open to a number of disadvantages [1]. Such small amounts of material can be determined with great accuracy if they are dealt with at the concentrations normally employed in macro-methods, by using correspondingly small volumes.

A method whereby this accuracy can be achieved is ultra-micro chemical analysis.

As indicated previously [2], all operations involving volumes of the order of 10^{-3} ml are carried out on the object stage of a microscope by means of manipulators which necessitate the use of specific apparatus.

Most published work on volumetric ultra-micro analysis is devoted to titrimetric determinations in volumes greater than 10^{-3} ml, in which microscope and manipulators are not used. Among work carried out along these lines, mention may be made of the work of I. M. Korenman and his coworkers [3,4]. They paid considerable attention to questions of the influence of the specific characteristics of ultra-micro volumetric analysis, and the consequent use of small volumes of test sample on the results of the determinations. A thiocyanate method [5] has been used for the micro-volumetric determination of silver in amounts of 2 – 15 μg. The use of the three basic methods of volumetric analysis (neutralization, oxidation-reduction, and precipitation) in ultra-micro methods is described in detail in the monograph by P. Kirk who systematized a large number of actual examples of various determinations [6].

Only one paper by A. Benedetti-Pikhler [1] is devoted to ultra-micro titration involving the use of microscope and manipulators. In this paper the final end point is determined by the color change of an indicator fixed on fine threads introduced into the solution.

Volumetric methods of ultra-micro analysis are used chiefly for the determination of the main components of very small samples of solid materials or solutions.

In view of the fact that the analytical principles of the ultra-micro method of chemical analysis do not differ from those of analysis of normal amounts of material [2], on switching over to ultra-micro chemical determinations, it is necessary to take into account all the data known about the reliability, advantages, and disadvantages of the method of analysis used. Thus errors arising during volumetric determinations involving the use of colored indicators, and also a number of technical errors are still pertinent when one

switches over to the ultra-microscopic scale; there are, however, a number of specific characteristics which must also be taken into account when working with micro-gram amounts of materials [3,6].

Potentiometric Ultra-Micro Titration

The use of electrometric methods for the determination of the end-point enables one to decrease, or even eliminate, drop errors and titration errors which are connected with the use of colored indicators. In this connection another advantage of physico-chemical methods becomes apparent; viz., that during electrometric titration it is possible to use dilute test and standard solutions. Great possibilities are opened up for ultra-micro analysis by the new method of high frequency titration which does not require the introduction of electrodes into the cell.

Of electrometric methods of titration which are widely used at present, the most convenient method is potentiometric titration, since it enables changes in ionic concentration to be observed directly during titration. A number of difficulties which are consequences of dealing with small volumes hinder the application of potentiometric analysis in ultra-micro volumetric analysis. These difficulties, however, are not insuperable. Thanks to the advantages which electrometric determinations have over indicator methods of determining the end-points in ultra-micro analysis, the time has now come to develop methods for carrying out potentiometric titration on a micro scale. Though success has already been attained in this field without the application of the microscope [6,9], there is no published work on the technique (the use of microscope and manipulators) whereby such determinations can be carried out more conveniently by using manipulators for handling the small volumes involved.

Apparatus and techniques are described below for carrying out potentiometric titrations under the microscope.

a) Apparatus.

The basic apparatus by means of which all ultra-micro determinations [2] are carried out has to be modified slightly in oder to carry out potentiometric titrations. This is the result of having to use four manipulators instead of the usual two, because more instruments are involved in this particular technique. The additional manipulators are arranged on the same plate (Fig. 1).

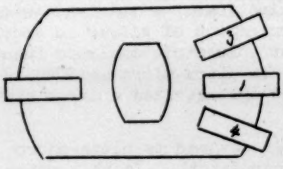


Fig. 1. The arrangement of manipulators during ultra-micro potentiometric determinations. 1, 2, 3, and 4 - manipulators.

The vessel in which potentiometric titration of small volumes is carried out is a small capillary (Fig. 2, a), 1 – 2 mm in diameter into which is fused a platinum wire b, one end of which serves as an electrode while the other end is connected via a mercury contact, c, and copper wire, d, to a potentiometer. The capillary is made in a micro-burner flame; the platinum wire is fused in and the capillary cut so that the working part of the capillary has an effective length of 3 – 4 mm. A drop of mercury is introduced into the opposite end of the capillary cut so that the working part of the capillary has an effective length of 3 – 4 mm. A drop of mercury is introduced into the opposite end of the capillary. The capillary is fixed with cement (3 parts rosin to 1 part paraffin wax) to one half of a piece of thick-walled capillary obtained by splitting the capillary along its axis. The glass holder with the capillary is fixed to the cover glass with the same cement.

Fig. 2. Titration capillary. a - Capillary; b - platinum wire; c - mercury contact; d - connecting wire.

Fig. 3. The reference electrode.

A calomel electrode (Fig. 2) may be used as reference electrode, the working part of which is a fine capillary with a tip 0.05-0.1 mm in diameter. It is filled by placing a drop of mercury and calomel paste into the vertical part of the electrode and filling it with a solution of potassium chloride through the capillary tip by means of a water pump. The tip is then filled with a solution of potassium chloride and agar-agar.

Mixing of the solution, which is essential during titration, is most conveniently carried out when working with a microscope by using a stream of inert gas, which on impinging on the surface of the solution creates turbulent motion throughout the whole volume of the solution. The gas stream is led through an ordinary glass tube fitted with a tap; the end of the tube is drawn out into a capillary.

The buret used for introducing the titrant into the capillary is itself a capillary with a diameter of about 0.5 mm. The end of the capillary is drawn out to a diameter of about 20μ. The capillaries for making burets are prepared in the flame of a micro-blow pipe from thick walled tubes with an external diameter of 6 - 8 mm and an internal diameter of 2 - 4 mm. The shape of the cross section of the capillaries thus obtained is checked under the microscope, using for this purpose an ocular scale (in the vertical position) or a drop of mercury (in the horizontal position). The buret tips are drawn out in a quartz micro-

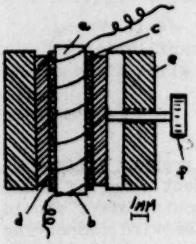


Fig. 4. Quartz micro-oven: a - quartz tube; b - nichrome winding; c - asbestos insulation; d - metallic body; e - metallic block for reinforcing the oven; f - clamping screw.

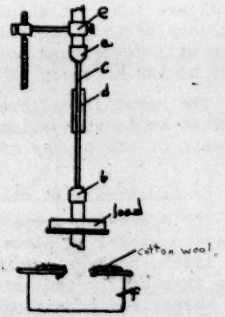


Fig. 5. Set-up for preparing microburets: a and b - clamps; c - capillary; d - quartz oven; e - reinforcement for the upper clamp; f - support.

oven (Fig. 4), which is connected to an AC supply through a rheostat and transformer (120 - 12 V). In order to draw out the tips thecapillaries are fixed in special clamps and fitted through the oven as shown in Fig. 5. That the internal diameter of the buret tip thus formed is correct is checked by means of an ocular scale. At that point of the buret where the diameter is the required one, an annular mark is made with a fine fibril of Canada balsam which has been heated beforehand. The buret is fixed in a micro-pipet holder [2], the opposite end of which serves for communicating with a leveling set-up (Fig. 6), which is used for creating pressure or rarefaction, respectively, counteracting or supporting the surface tension forces in the buret. In order to measure out a definite volume of titrant under these conditions, it is essential that the mark on the buret should be in the field of vision of the microscope. This is not always convenient. It is expedient, therefore, to use a buret constructed in the same way as the micro-pipet used in qualitative ultramicro analysis [2], but which enables the solution to be measured out accurately. For this purpose a pressure micrometer, b, is inserted in the piston apparatus between the holder, c, and the micro-screw, a, the movable part of the micrometer operating as a piston in the holder (Fig. 7). In such a buret a certain number of divisions read off

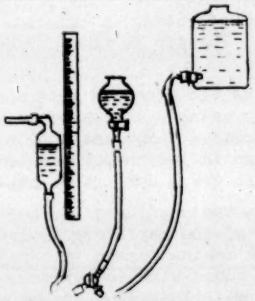


Fig. 6. Leveling assembly.

Fig. 7. Buret with pressure micrometer. a - Micro-screw; b - pressure micrometer; c - buret holder; d - buret.

by the needle on the micrometer dial for one turn of the screw corresponds to a definite volume of solution in the buret; this number is easily determined by calibration. It should be noted that the piston diameter should be cut down considerably (down to 1 mm); otherwise one scale division of the micrometer will correspond to too large a volume of solution expelled from the buret, so the accuracy of the reading is lowered.

The buret is calibrated by means of standard capillaries [1]; calculations are made as to what volume of liquid in a buret of given diameter does one scale division of the ocular micrometer correspond.

b) Procedure for Titration.

The apparatus prepared as described above is arranged as follows: the titration vessel is placed in a damp box on the object stage of a microscope (the little holders containing the titrant and reagents, etc., should also be in this box); the thick walled capillary with the wire connecting titration vessel and potentiometer is fixed in the left-hand manipulator; the micro-pipet (and subsequently the calibrated micro-buret) is fixed in the clamp of the right-hand manipulator; the reference electrode in the third manipulator; and the stirring device in the fourth.

The calomel electrode is introduced into the damp box with the help of the manipulator. While observing this under the microscope, the manipulator

rack is turned and a position is found for the tip of the calomel electrode such that it is arranged along the horizontal axis and is in the center of the field of vision. The titration vessel is then adjusted with respect to the tip of the calomel electrode until the electrode tip is in one half of the titration vessel. In this position, by observing with the naked eye, the wire connecting the titration cell to the potentiometer is fitted to the other end of the titration vessel by means of the left hand manipulator. In this way the mutual positions of the parts of the apparatus most difficult to coordinate are established. The only motions necessary to be made with the respective manipulators after establishing this position are then backwards and forwards.

With the left manipulator the end of the wire connecting titration vessel with the potentiometer is withdrawn, and the vessel itself is drawn back, thereby freeing the end of the calomel electrode, which is removed from the field of vision. The tip of the calomel electrode is then moved away to a certain distance and is arranged in a position parallel to its original position.

The titration vessel is now brought back into the field of vision arranging it so that its open end is almost at the opposite side of the field of vision along the center, and by observation through the microscope a position is found for the fourth manipulator such that the tip of the capillary which serves as the stirrer (the gas capillary) is brought up to the opening of the vessel and arranged along its axis. The manipulator used for handling the gas capillary is then pulled away, and the gas capillary fixed in a position parallel to that which it had under the microscope.

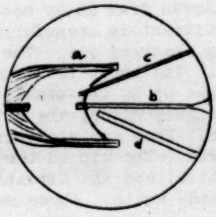


Fig. 8. Arrangement of the apparatus during titration (view under the microscope). a - Vessel; b - buret; c - calomel electrode; d - capillary for leading in the gas for stirring.

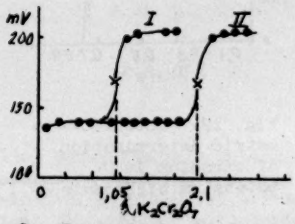


Fig. 9. Potentiometric determination of iron in Mohr's salt.
I - $1 \cdot 10^{-3}$ ml solution; II - $2 \cdot 10^{-3}$ ml solution.

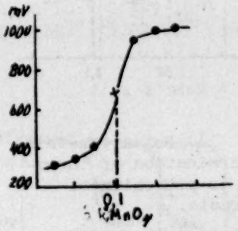


Fig. 10. Potentiometric determination of iron in Mohr's salt.

One of the vessels kept in the damp box in its holder is brought into the field of vision and filled with the solution to be titrated by means of the micro-pipet. From this vessel a known volume of solution is transferred to the titration vessel. Using the same micro-pipet after first having washed it out with water and the titrant, another vessel in the damp box is filled with titrant. Instead of this micro-pipet, the calibrated buret with the pressure is now fitted into the right hand manipulator. The tip of the calomel electrode is brought into the field of vision and arranged along the center. The titration flask is moved on to it until the tip of the electrode is in the solution. The opposite end of the titration flask is connected to the potentiometer. Measurements are made. Subsequently the above manipulations are repeated, and the connecting wire and the calomel electrodes are withdrawn. The vessel containing the titrant is now brought into the field of vision, and titrant is withdrawn from it by means of the buret which is evacuated by means of the piston. The titrant is transferred to the titration vessel, a definite volume of titrant being measured out. The amount is determined by the reading on the micrometer dial. The buret is withdrawn from the field of vision, and the gas capillary brought up to the titration vessel. The contents of the titration vessel are thoroughly mixed, the motion of the solution being observed under the microscope. They are withdrawn from the field of vision, and the gas capillary also removed. The tip of the calomel electrode is once more introduced into the solution, and the titration flask connected to the potentiometer. Measurements are made again. These manipulations are repeated until titration is complete.

The general arrangement of the apparatus during titration is shown in Fig. 8.

Titrations involving the use of a buret worked by means of a leveling device is carried out in exactly the same way, the only difference being that when adding a definite volume of titrant, the mark on the buret [1] is kept in the field of vision.

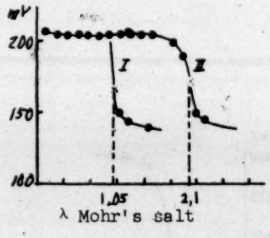


Fig. 11. Potentiometric determination of chromium in potassium bichromate.

I) $1 \cdot 10^{-3}$ ml solution;

II) $2 \cdot 10^{-3}$ ml solution.

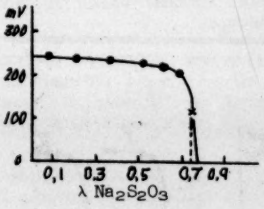


Fig. 12 Potentiometric determination of chromium in potassium bichromate.

TABLE 1

Determination of Iron in Mohr's Salt

Titrant Solution	Concentration in N	Amount used in ml	Solution of Mohr's salt titrated		Amount of iron in g		Error in %
			Volume in ml	Concentration in N	Taken	Found	
$K_2Cr_2O_7$	0.01	$1.99 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	0.01	$1.12 \cdot 10^{-6}$	$1.11 \cdot 10^{-6}$	- 0.5
$K_2Cr_2O_7$	0.01	$1.01 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	0.01	$0.56 \cdot 10^{-6}$	$0.566 \cdot 10^{-6}$	+ 1.0
$KMnO_4$	0.10	$0.102 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	0.01	$0.56 \cdot 10^{-6}$	$0.57 \cdot 10^{-6}$	+ 2.0

TABLE 2

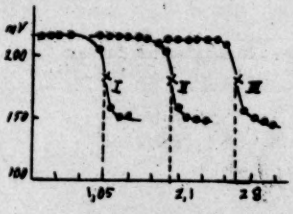
Determination of Chromium in Potassium Bichromate

Titrant Solution	Concentration in N	Amount used in ml	Solution of $K_2Cr_2O_7$ titrated		Amount of chromium in g		Error in %
			Volume in ml	Concentration in N	Taken	Found	
Mohr's salt	0.01	$1.98 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	0.01	$3.46 \cdot 10^{-7}$	$3.43 \cdot 10^{-7}$	- 1.0
" "	0.01	$1.002 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	0.01	$1.73 \cdot 10^{-7}$	$1.733 \cdot 10^{-7}$	+ 0.2
$Na_2S_2O_3$	0.10	$0.76 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	0.01	$2.91 \cdot 10^{-6}$	$3.0 \cdot 10^{-6}$	+ 3.0

TABLE 3

Determination of Vanadium in Ammonium Vanadate

Titrant Solution	Concentration in N	Amount used in ml	Solution of NH_4VO_3 titrated		Amount of vanadium in g		Error in %
			Volume in ml	Concentration in N	Taken	Found	
Mohr's salt	0.01	$2.91 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	0.01	$1.53 \cdot 10^{-6}$	$1.48 \cdot 10^{-6}$	- 3.0
" "	0.01	$1.96 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	0.01	$1.02 \cdot 10^{-6}$	$0.999 \cdot 10^{-6}$	- 2.0
" "	0.01	$1.023 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	0.01	$5.1 \cdot 10^{-7}$	$5.22 \cdot 10^{-7}$	+ 2.3



λ Mohr's salt

Fig. 13. Potentiometric determination of vanadium in ammonium vanadate. I - $1 \cdot 10^{-3}$ ml solution; II - $2 \cdot 10^{-3}$ ml solution; III - $3 \cdot 10^{-3}$ ml solution.

Potentiometric Ultra-micro Determination

Using the apparatus developed for ultra-micro titration, a number of determinations were carried out which demonstrated the possibilities of the method.

Solutions of known concentration were made in 5 ml standard flasks and aliquots taken. A PPT-1 potentiometer was used in conjunction with a galvanometer of sensitivity 10^{-8} A.

Results for determinations of iron in Mohr's salt, chromium in potassium bichromate, and vanadium in a sulfuric acid solution of ammonium vanadate are adduced in Tables 1, 2, and 3; the corresponding curves are given in Figs. 9, 10, 11, 12, and 13. A determination takes about 15 – 20 minutes.

SUMMARY

1. Apparatus and techniques have been worked out for potentiometric ultra-micro titration under the microscope.

2. Potentiometric ultra-micro determinations of 10^{-6} – 10^{-7} g of material in volumes of ca. 10^{-3} ml are described.

3. The results obtained are of a fairly high accuracy and their reproducibility is good.

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SPECTROGRAPHIC STUDY OF REACTIONS OF IMPORTANCE IN COLORIMETRY

I. COMPLEX COMPOUNDS FORMED BY NICKEL IONS WITH SODIUM-2-NITROSO-1-NAPHTHOL-4-SULFONATE

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1-Nitroso-2-naphthol and 2-nitroso-1-naphthol and their derivatives find wide use in colorimetric analysis for the determination of cobalt and other ions. We have already studied complex formation between cobalt and 1-nitroso-2-naphthol [1], and with sodium-1-nitroso-2-naphthol-3,6-disulfonate[nitroso-R-salt] [2], and also with other nitroso naphtholate derivatives.

In this paper we give results of our study of complex formation between nickel ions and sodium 2-nitroso-1-naphthol-4-sulfonate[nitroso-N-salt].

This compound was suggested by Sarver [3], as a qualitative reagent for cobalt. This reagent also gives colors with nickel, copper, and iron ions. No indications of the composition of the colored compounds formed are given in Sarver's paper, nor any information about their stability. Neither is there information on these points in articles published recently [4,5].

We prepared nitroso-N-salt by Witt and Kaufmann's method[1)][6], and purified it by recrystallization from water. This was followed by washing with alcohol. Aqueous solutions of this reagent remain unchanged over long periods. All optical density measurements of the solutions were made with a spectrodensograph [7]. Hydrogen ion concentration was controlled by means of the quinhydrone electrode, in some cases with a glass electrode.

Fig. 1 illustrates absorption curves for solutions containing $6.21 \cdot 10^{-4}$ mol/liter nitroso-N-salt, and $2.07 \cdot 10^{-4}$ mol/liter nickel ions at various pH's.

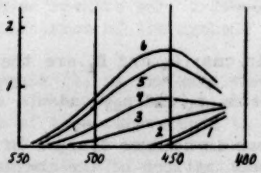

Fig. 1. Relation between optical density and pH. 1 - pH 2; 2 - pH 3; 3 - pH 4; 4 - pH 5; 5 - pH 6; 6 - pH 7-10.

Preliminary tests showed that the reaction between nickel and nitroso-N-salt practically finishes as soon as the solutions are mixed. The optical densities of solutions of constant pH but of different buffer mixtures differ from each other. As a result it was decided that in further work buffer mixtures would not be used and the pH would be adjusted by means of acid (HCl) or alkali (NaOH), the pH being controlled potentiometrically.

It is clear from Fig. 1 that on changing the pH from 2 to 10, the optical density, D, increases appreciably, tending to a limiting value. It is noteworthy that even at a pH of 10 no formation of nickel hydroxide occurs, although the nitroso-N-salt is not present in excess in this experiment. This testifies to the high stability of the colored complex.

1) For convenience nitroso-N-salt is abbreviated still further to RN.

In order to determine the stoichiometric coefficient in the equation for complex formation, we used Ostromyslensky's method [8] as modified by N. P. Komar [9]. Experiments were carried out at pH's of 4, 5, and 6. Measurements were made at λ = 450, 480, 500, and 520 mμ. The initial equimolar concentration of nickel ions and complexing agent was 8.27×10^{-4} in the first series, and 2.8×10^{-4} in the second series. Fig. 2 illustrates curves for ΔD composition of mixtures, where ΔD is the difference between the measured optical densities and the corresponding values for solutions of pure nitroso-N-salt for a given composition. We have only given results for one wave-length and for an initial concentration of $c_{Ni^{2+}} = c_{RN} = 8.27 \times 10^{-4}$ mol/liter. The thickness of the colored layer was l = 0.5 cm.

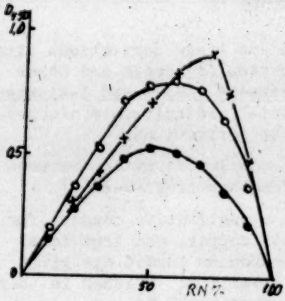

Fig. 2. Determination of composition:
-●-●- at pH 4;
-o-o- at pH 5;
-x-x- at pH 6.

The four series of tests at pH 4, two series at pH 5, and two series at pH 6 showed that the ratios of $c_{Ni^{2+}}:c_{RN}$ at the maximum of the curve ΔD-composition are respectively 1:1, 1:2 and 1:3. Further experiments were carried out along these lines at definite, fixed pH's.

First of all, the equilibrium at pH ≤ 4 was studied. Three series of tests were made at pH 3.5 by the method developed by Komar[10]. In all the experiments the ratios of the initial concentrations remained constant and equal to 1:1. The absolute value of the concentration varied from 4.14×10^{-4} to 1.65×10^{-4} mol/liter.

On the basis of the measured optical densities at λ=480 and 500 mμ, the molar absorption coefficients, ϵ_λ, were calculated by means of Komar's formula, which is suitable in cases of the formation of compounds with a composition of 1:1.

$$\epsilon_\lambda = \frac{1}{l} \frac{D_i - nD_k}{c_i - nc_k}, \qquad (1)$$

where l is the thickness of the colored layer in cms; D_i and D_k are the optical densities of solutions with initial concentrations, c_i and c_k; and $n = \sqrt{\frac{D_i}{D_k}}$.

Statistically treated values of ϵ_λ are shown in columns 1 and 2 of Table 1. By means of these coefficients, equilibrium concentrations of the complex (z mols/liter) were calculated, and from these, the equilibrium constant of the complex formation reaction. In writing these reactions, one must initially take into account two possible variants of the equilibrium; in the first of these variants the following reactions are considered:

$$RN \rightleftarrows R^- + N^+ \qquad K_1; \qquad (2)$$

$$Ni^{2+} + R^- \rightleftarrows NiR^+ \qquad K_2 \qquad (3)$$

while in the second variant the following equation is also included:

$$Ni^{2+} + H_2O \rightleftarrows NiOH^- + H^+ \qquad (4)$$

In the first variant the overall process can be depicted by the equation:

$$Ni^{2+} + RN \rightleftarrows NiR^{+} + N^{+}, \quad (5)$$

for which

$$K_I = K_1 \cdot K'_2 = \frac{[NiR^{+}][N^{+}]}{[Ni^{2+}][RN]} = \frac{z}{(c - z)^2} \cdot h, \quad (6)$$

while in the second

$$Ni^{2+} + RN + H_2O \rightleftarrows NiRON + 2H^{+}, \quad (7)$$

for which

$$K_{II} = \frac{[NiRON][H^{+}]^2}{[Ni^{2+}][RN]} = \frac{z}{(c - z)^2} \cdot h^2, \quad (8)$$

where $z = [NiR^{+}]$ or $[NiRON]$, $c - z = [Ni^{2+}] = [RN]$, $h = [N^{+}]$, $c = c_{Ni^{2+}} = c_{RN}$

Calculations gave: $K_I = 0.74$ and $K_{II} = 2.30 \times 10^{-4}$. Results of statistical treatment of the mean value of K_I are adduced in Table 1, column 3.

TABLE 1

Results of the Statistical Treatment of Data Obtained during Calculations of the Molar Extinction Coefficients and Equilibrium Constants

Expt. No.	Calculated value	Mean value	No. of experiments, n	Dispersion S^2	Mean square error $S_{\bar{x}}$	t_α	$\pm t_\alpha S_{\bar{x}}$	Relative error, in %
1	ϵ_{480}	3240	21	1.7×10^6	287	2.09	596	18
2	ϵ_{500}	2800	21	1.3×10^6	252	2.09	530	19
3	K_I	0.74	26	1.7×10^{-2}	2.6×10^{-2}	2.06	5.4×10^{-2}	7
4	ϵ_{480}	3680	10	1.0×10^4	33	2.26	75	2
5	ϵ_{500}	2960	10	5.5×10^4	74	2.26	167	6
6	K_I	0.65	26	4.9×10^{-3}	1.2×10^{-2}	2.06	3×10^{-2}	4
7	ϵ_{500}	8650	20	3.1×10^5	124	2.09	260	3
8	ϵ_{510}	7370	20	4.9×10^5	156	2.09	330	5
9	K_{III}	3.63×10^{-5}	20	7.1×10^{-10}	5.9×10^{-6}	2.09	1.23×10^{-5}	33

Note. These results were treated by methods described in [12, 13]. Vide ibid. the significance of the symbols S^2, $S_{\bar{x}}$, t_α and $\pm t_\alpha S_{\bar{x}}$.

Formula (1) is the same for calculations of ϵ_λ at constant pH for both variants of the equilibrium, so that it is impossible to decide the question as to which of them corresponds to actual fact, (5) or (7), on the basis of calculations of ϵ_λ. In order to solve this problem, experiments were made at different pH values (within the limits 3.0 – 4.0) with mixtures of constant composition 1:1. In all the mixtures, $c_{Ni^{2+}} = c_{RN} = 8.27 \times 10^{-4}$ mols/liter. Optical densities ($D_{measured}$) were measured for different wave lengths. Using the molar extinction coefficients obtained earlier and the values of the constants K_I and K_{II}, the optical densities ($D_{calculated}$) were calculated for the same conditions; these were compared with $D_{measured}$. As shown in Fig. 3, $D_{calculated}$ follows changes in $D_{measured}$ satisfactorily only for the first variant of the equilibrium ($K_I = 0.74 \pm 0.05$). The fact that at a pH of 4 the hydrolysis of Ni^{2+} ions is completely insignificant, as can be easily calculated on the basis of the hydrolysis constant $K_3 = 5 \times 10^{-10}$ [11], is an indirect confirmation of this result.

A convincing proof of the existence of one complex of composition 1:1 at pH < 4 is given by experiments on the determination of ϵ_λ by the "saturation

method' in excess Ni^{2+} ions. Optical densities were measured for a wide wave length range at pH's of 3.3 and 3.8 for solutions containing various concentrations of RN and a constant concentration of Ni^{2+} ions which ensured a practically complete shift of equilibrium (5) to the side of the formation of the complex NiR^+.

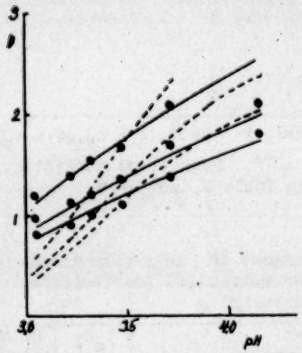

Fig. 3. Establishment of equilibrium type:
- - - calculated from K_{II} values;
——— calculated from K_I values;
• • • experimental values of D.

Corrections were applied to the values of D_λ for the characteristic color of Ni^{2+} ions, and ϵ_λ for the complex calculated on the basis of Beer's law. Columns 4 and 5 of Table 1 contain statistically treated mean values of $\bar{\epsilon}_\lambda$ for two wave lengths; they are similar to values of ϵ_λ obtained under equilibrium conditions (columns 1 and 2) and have a smaller error. We used these coefficients to calculate more reliable K_I values, the average value of which was: $\bar{K} = 0.65 \pm 0.03$. Statistically treated results are given in column 6, Table 1. "Saturation" experiments enable us to construct an absorption curve for a complex having a composition 1:1 (see Fig. 4, Curve 1).

In so far as $K_I = K_1 \cdot K'_2 = 0.65$ and $K_1 = 8.2 \times 10^{-7}$, then the constant of complex formation $K'_2 = 7.9 \times 10^5$, while the instability constant $K_2 = 1.3 \times 10^{-6}$.

Further experiments were made at pH $\geqslant 6$. Under these conditions complex formation can be schematically represented by the equations:

$$RN \rightleftarrows R^- + N^+ \qquad K_1; \qquad (2)$$

$$Ni^{2+} + 3R^- \rightleftarrows NiR_3^- \qquad K'_4; \qquad (9)$$

or in general:

$$Ni^{2+} + 3RN \rightleftharpoons NiR_3^- + 3N^+ \qquad III, \quad (10)$$

$$K_{III} = \frac{[NiR_3^-][N^+]^3}{[Ni^{2+}][RN]^3} = \frac{t \cdot h^3}{27(c-t)^4},$$

if $c_{RN} = 3c_{Ni^{2+}}$. Here $t = [NiR_3^-]$. In the case considered, formula (1) for calculation of ϵ_λ contains $n = \sqrt[4]{\frac{D_i}{D_k}}$.

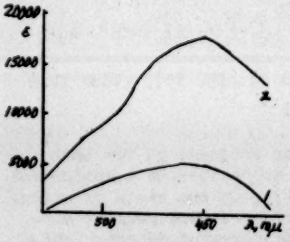

Fig. 4. Absorption curves: 1 - complex NiR^+, 2 - NiR_3^-

Two series of experiments were carried out at pH 6. In all the mixtures $c_{RN} = 3c_{Ni^{2+}}$. Optical densities were measured at $\lambda = 500$ and 510 mμ, and on the basis of these results, ϵ_λ was calculated first by means of formula (1), followed by calculation of K_{III}. Table 1 contains the results of statistical treatment of $\bar{\epsilon}_\lambda$ (columns 7 and 8) and K_{III} (column 9). $\bar{K}_{III} = (3.6 \pm 1.2) \times 10^{-5}$.

In so far as $K_{III} = K_1^3 \cdot K'_4 = 3.6 \times 10^{-5}$, while $K_1 = 8.2 \times 10^{-7}$, then $K_4 = 0.65$ while the instability constant $K'_4 = 1.5 \times 10^{14}$.

The presence of two complexes with composition 1:1 and 1:3 complicates the use of simple methods of calculating for the determination of the properties of a possible complex with a composition of 1:2. The actual existence of this complex is in doubt since, in the presence of two other complexes, comparatively close to each other with respect to their optical results, the maximum observed on the Ostromyslensky-Job diagram at pH 5 may be a simple consequence of the superimposition of these two other complexes.

Let us assume that there are only two complexes of the composition 1:1 and 1:3 in the system under examination; then one can write the following equilibrium system:

$$Ni^{2+} + RN \rightleftarrows NiR^{+} + N^{+} \qquad K_I \qquad (5)$$

$$NiR^{+} + 2RN \rightleftarrows NiR_3^{-} + 2N^{+} \qquad K \qquad (11)$$

$$Ni^{2+} + 3RN \rightleftarrows NiR_3^{-} + 3N^{+} \qquad K_{III} \qquad (10)$$

from which

$$K = \frac{K_{III}}{K_I} = 5.6 \times 10^{-5} \qquad (12)$$

Here $[Ni^{2+}] = x$, $[RN] = y$, $[NiR^{+}] = z$, and $[NiR_3^{-}] = t$ are unknown, while $[N^{+}] = h$ is known. Four equations can be written:

$$zh = K_I xy; \qquad (13)$$

$$th^2 = Kzy^2; \qquad (14)$$

$$a = x + z + t; \qquad (15)$$

$$b = y + z + 3t, \qquad (16)$$

where $a = c_{Ni^{2+}}$, and $b = c_{RN}$

By substituting the values of z and t from equations (13) and (14) in equations (15) and (16), and making a simple transformation, we get the equation:

$$\frac{KK_I}{h^3} y^4 + \left(\frac{3aKK_I}{h^3} - \frac{KK_I b}{h^3} \right) y^3 + \frac{K_I}{h} y^2 + \left(1 + \frac{K_I a}{h} - \frac{K_I b}{h} \right) y - b = 0, \qquad (17)$$

by means of which it is possible to calculate $y = [RN]$, and therefrom all the remaining equilibrium concentrations.

Six mixtures were made up in which $c_{Ni^{2+}} = a = 2.07 \times 10^{-4}$ mol/liter, $c_{RN} = b = 6.21 \times 10^{-4}$ mol/liter, while the pH was varied from 2.0 to 7.0. Optical densities were measured at $\lambda = 500$ and 510 mμ. Using the known values of K_I, K, h, a and b, the coefficients of y in equation (17) were then calculated and from these the values of y, x, z, and t. Results of measurements and calculations are adduced in Table 2, while the corresponding graphs are given in Fig. 5. Knowing the equilibrium concentrations of the complexes and using the molar extinction coefficients obtained, it is not difficult to calculate the optical densities and compare them with the experimental values. Table 2 shows that the calculated values are in good agreement with measured ones, which testifies to the correctness of our assumption re the existence of only two complexes in the system under examination.

D_λ was measured in a wide wave length range for solutions of pH 7. From the values of D_λ found, optical densities d_λ corresponding to the absorption

TABLE 2

Results of Calculations of Equilibrium Concentrations in Relation to pH

$c_{Ni^{2+}} = a = 2.07 \times 10^{-4}$ mol/liter,

$c_{RN} = b = 6.21 \times 10^{-4}$ mol/liter.

Expt. No.	pH	[RN] y	$[Ni^{2+}]$ x	$[NiR^+]$ z	$[NiR_3^-]$ t	D_{500}		D_{510}	
						Calculated	Measured	Calculated	Measured
1	2.03	6.10×10^{-4}	1.99×10^{-4}	8.43×10^{-6}	2.02×10^{-12}	–	–	–	–
2	3.00	5.62×10^{-4}	1.52×10^{-4}	5.54×10^{-5}	9.73×10^{-10}	–	–	–	–
3	3.95	4.72×10^{-4}	5.56×10^{-5}	1.52×10^{-4}	1.44×10^{-7}	0.22	0.20	0.16	0.15
4	5.00	4.23×10^{-4}	6.64×10^{-6}	1.83×10^{-4}	1.79×10^{-5}	0.35	0.38	0.25	0.30
5	6.00	1.60×10^{-4}	8.16×10^{-7}	8.52×10^{-5}	1.21×10^{-4}	0.65	0.70	0.53	0.55
6	7.00	3.01×10^{-5}	1.66×10^{-7}	3.30×10^{-5}	1.73×10^{-4}	0.80	0.80	0.68	0.65

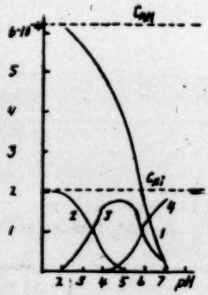

Fig. 5. Calculated equilibrium concentrations: 1 - [RN]; 2 - $[Ni^{2+}]$; 3 - $[NiR^+]$; 4 - $[NiR_3^-]$.

of complex NiR^+ were calculated, the concentration of the complex at this pH $[NiR^+] = 3.3 \times 10^{-5}$, while ϵ_λ values are adduced in Fig. 4. The difference $(D_\lambda - d_\lambda)$ is used for calculating ϵ_λ for the complex NiR_3^-. Results of calculations are adduced in the form of a graph (curve 2) in Fig. 4.

The complex NiR^+ is probably an ordinary inner-complex compound, in which the second valency of the Ni^{2+} ion remains in the ionized state. It is more difficult to decide this point for the somewhat unusual complex for bivalent nickel, NiR_3^- – whether it can be regarded as an inner complex compound. It may be that in this particular instance we are dealing with an acido-complex. We cannot completely reject the possibility of the formation of an actual inner complex compound, NiR_2. Experiment has only indicated that the concentration of such a complex, if there is one, does not exceed 3 – 4% of the total concentration of all particles in solution; i.e., it is within the limits of experimental error for the determination of optical density.

SUMMARY

1. It has been established that two complexes, NiR^+ and NiR_3^-, are formed in solutions containing Ni^{2+} ions and 2-nitroso-1-naphthol-4-sulfonate in accordance with the pH value.

2. The molar extinction coefficients of these complexes have been calculated, as well as their instability constants. For NiR^+, $K_2 = 1.3 \times 10^{-6}$, and for NiR_3^-, $K_4 = 1.5 \times 10^{-14}$.

3. The NiR_3^- complex is fairly stable in solution up to a pH of 10, and has high values for the molar extinction coefficients, which may be of interest for

the colorimetric and spectrophotometric determination of nickel.

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THE APPLICATION OF THE ULTRA-VIOLET IN ANALYTICAL CHEMISTRY

CERIMETRY IN THE ULTRA-VIOLET

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Solutions of quadrivalent cerium are known to possess a number of valuable properties [1, 2, 3] as compared with the widely used potassium permanganate: 1) acid solutions are very stable and maintain their normality over a long period, 2) they do not decompose on boiling for over an hour, 3) reduction proceeds without intermediate steps.

Determination of equivalence points during cerimetric titration in the ultra-violet is based on a sharp change in absorption at the transition $Ce^{IV} \rightarrow Ce^{III}$; quadrivalent cerium ions exhibit a very strong ultra-violet absorption at 356 $m\mu$, while trivalent cerium ions are completely transparent at this wave-length [4]. The method of determination does not differ from that used in previous work [5]. A more refined apparatus which we have constructed is used in this work instead of the ultra-chemiscope.

Having studied the conditions for determining the equivalence point in the ultra-violet of oxidation reduction reactions which are accompanied by the formation of compounds which are colorless in the ultra-violet, we came to the conclusion that the ultra-chemiscope could only be used when the material to be titrated has a very large absorption coefficient and very sharp absorption limits in the part of the spectrum used for absorption. The most suitable part of the spectrum for titration is at 365 $m\mu$ since ultra-violet rays of shorter wave length are absorbed by most chemical compounds. The use of an apparatus which gives ultra-violet rays of all wave lengths (including the short ones) for titration is, therefore, restricted. In the case of compounds which have diffuse absorption limits in the ultra-violet; i.e., those materials which, in addition to absorbing at $\lambda = 365$ $m\mu$, also absorb light of shorter wave lengths; a delayed onset of the titration end point is observed. On titration to darkening; i.e., to the appearance of absorption, the end point is observed sooner. Similar phenomena become apparent when fluorescent screens are excited not only by one particular band in the ultra-violet, but are also partially excited by others; e.g., uranium glass is excited by $\lambda =$ 313 and 254 $m\mu$ as well as by $\lambda = 365$ $m\mu$.

It is known [6] that many compounds in solution, on irradiation with ultra-violet rays, undergo photo-chemical decomposition, and this may serve as an additional source of error during titration. As a rule the photo-reduction effect increases with increasing extinction coefficient and appears to be greatest at the maximum absorption of the ultra-violet [4]; i.e., to a greater extent in the short wave length region (313 - 254 $m\mu$). Thus the presence of short wave lengths in the pencil of rays isolated by an UFS-1 light filter of the ultra-chemiscope, increases photochemical decomposition which becomes observable with time (it becomes most apparent when titration of test material takes 5 - 10 minutes).

On carrying out an oxidation-reduction titration; e.g., of a solution of ferric chloride with ascorbic acid, hydrogen peroxide, cerium sulfate (IV), etc., we observed a premature (though with only a small deviation) onset of the titration end point, which could only be explained by photo-chemical reduction

of part of the solution being titrated.

In addition, the use of quartz cuvettes for titration also favors increased photo-reduction of the solution to be titrated as has been shown by Dain and Kachan [6], using the reduction of Ce^{IV} ions as an example. The quartz walls of the cuvette catalyzed photo-reduction considerably.

In order to achieve more accurate results, therefore, it is essential during titration to isolate that part of the spectrum to be used more monochromatically than can be done by means of the ultra-chemiscope; ultra-violet of λ = 313 mμ or less must be completely absent. The isolation of a particular part of the ultra-violet is of particular importance when there are other substances present which can absorb in the 313 – 254 mμ region.

We carried out titration, therefore, using the UFS-3 light filter which has maximum transmission at 365 mμ; i.e., at that part of the spectrum which is most useful for volumetric work. By using this light filter, we avoided errors arising from the absorption of shorter ultra-violet rays. Moreover the photo-chemical processes of reduction become practically insignificant since the absorption maxima of most of the substances participating in the reactions used for oxidation-reduction titration lie at wave lengths considerably shorter than 365 mμ. We also used ordinary chemical beakers instead of quartz cuvettes since practically no light of wave length λ = 365 mμ is absorbed by a thin layer of ordinary glass. With these modifications we got an apparatus which is extremely useful for volumetric analysis. All the examples of cerimetric titration described below were carried out with this apparatus.

Solutions of cerium sulfate (IV) in 1 N sulfuric acid were used in the present work. The scale divisions of the buret used were 0.005 ml.

EXPERIMENTAL

Titration of Oxalates with Cerium Sulfate (IV)

Cerium sulfate (IV) reacts with sodium oxalate as follows:

$$2Ce(SO_4)_2 + Na_2C_2O_4 = Ce_2(SO_4)_3 + 2CO_2 + Na_2SO_4.$$

The equivalence point is usually determined potentiometrically during cerimetric titration of oxalates. A visual method [7] is also known, but it is not easy to carry out since it requires preliminary preparation of ClI catalyst for speeding up the reaction, and also the presence of an indicator: the yellow color of cerium sulfate (IV) is not intense enough for fixing the end point.

TABLE 1

Amount of $C_2O_4^{2-}$ taken, in mg	Amount of $C_2O_4^{2-}$ found, in mg	Error, in mg
65.295	65.293	-0.002
65.295	65.299	+0.004

Titration in the ultra-violet permits the equivalence point to be determined visually without introducing catalyst or indicator. The determination is based on the difference in absorption in the ultra-violet at λ = 365 mμ of cerium sulfate (IV) and cerium sulfate (III). At the equivalence point a shadow appears on the screen which is a result of the presence of excess cerium sulfate (IV) in solution. The oxalate which is formed as the result of the reaction with sodium oxalate, and the sulfuric acid present in solution do not absorb in the ultra-violet at this wave length [8]. The solution of oxalate to be titrated is heated beforehand to 90° and 5 ml of sulfuric acid (1:5) added to prevent precipitation of cerium sulfate. Results of titrations are given in Table 1.

It is evident from the table that the experimental error is very small. The method can be used for preparing standard solutions of cerium sulfate (IV).

Titration of Antimony Trichloride with Cerium Sulfate (IV)

Cerium sulfate (IV) reacts with antimony trichloride according to the equation:

$$Ce(SO_4)_2 + SbCl_3 + 2HCl = Ce_2(SO_4)_3 + SbCl_5 + H_2SO_4.$$

Willard and Young [2] used this reaction for electrometric titration. Rathsburg [9] has checked on the possibility of a visual titration of antimony trichloride with cerium sulfate (IV); he used methylene blue, methyl orange, and methyl red as indicators.

We checked the titration of antimony trichloride with cerium sulfate (IV) in the ultra-violet. We showed that the reaction between antimony trichloride and cerium sulfate (IV) only follows the above equation when both solutions to be titrated are 1 N with respect to sulfuric acid. In this case the reaction is rapid and the end point is easily fixed by the appearance of a shadow on the luminescent screen. When the concentration of sulfuric acid is high, the solution starts to absorb the ultra-violet immediately after the addition of a few drops of cerium sulfate (IV) to the antimony trichloride. It is probable that the antimony chloride formed as the result of the reaction forms a compound with sulfuric acid in strongly acid media which absorbs the ultra-violet at 365 mμ. Hydrochloric acid in any concentration does not interfere with the antimony determination. Titration results are given in Table 2.

TABLE 2

Sb taken, in mg	Sb found, in mg	Error, in mg
25.437	25.420	− 0.017
25.437	25.417	− 0.020

Titration of Sodium Arsenite with Cerium Sulfate (IV)

The following reaction lies at the basis of the interaction between sodium arsenite and cerium sulfate (IV):

$$Ce(SO_4)_2 + Na_3AsO_3 + H_2O = Ce(SO_4)_3 + Na_3AsO_4 + H_2SO_4.$$

Willard and Young [2] carried out a visual determination of sodium arsenite with cerium sulfate (IV) in the visible spectrum using ClI as a catalyst and methylene blue as indicator.

Titration in the ultra-violet was carried out as follows: the arsenite solution was heated to 90°, and to the hot solution was added a solution of cerium sulfate (IV) until a shadow appeared on the luminescent screen, indicating the end point. Titration results are adduced in Table 3.

TABLE 3

As taken, in mg	As found, in mg	Error, in mg
16.094	16.074	− 0.020
16.094	16.078	− 0.016

Titration of Stannous Chloride with Cerium Sulfate (IV)

The most frequently used volumetric method of determining stannous chloride is the iodometric method. Nevertheless because of the volatility of iodine, titration in the presence of starch, and the easy oxidizability of stannous chloride by atmospheric oxygen, the errors of this method are considerable.

TABLE 4

Sn taken, in mg	Sn found, in mg	Error in mg
28.766	28.736	− 0.030
28.766	28.732	− 0.034

Colorimetric titration of stannous chloride in the ultra-violet eliminates the first two sources of error: the working solution is a stable solution of cerium sulfate (IV), while the end point is indicated by absorption of the ultra-violet by the solution as the result of the appearance of excess cerium sulfate

(IV). Oxidation by atmospheric oxygen can be avoided by carrying out the titration of stannous chloride in a carbon dioxide atmosphere.

Stannous chloride and cerium sulfate (IV) react in acid media as follows:

$$2Ce(SO_4)_2 + SnCl_2 + 2HCl = Ce_2(SO_4)_3 + SnCl_4 + H_2SO_4.$$

Hydrochloric and sulfuric acids as well as $SnCl_2$ and $SnCl_4$ are transparent to the ultra-violet at the wave length employed in titration (365 mμ). Absorption, as in previous examples, is solely shown by cerium sulfate (IV). Titration results are given in Table 4.

Titration of $SnCl_2$ and Na_3AsO_3 When Both Are Present Together

Determination of $SnCl_2$ and Na_3AsO_3 when present together is possible on the following grounds: the normal oxidation potential of the system $Ce^{IV} + e \rightleftharpoons Ce^{III}$ is + 1.55 V; of the system $Sn^{II} - 2e \rightleftharpoons Sn^{IV}$ is + 1.54 V; and of the system $H_3AsO_3 + H_2O - 2e \rightleftharpoons H_3AsO_4 + 2H^+$, + 0.574 V. Accordingly stannous chloride will be first titrated in solution, followed by the arsenite, since the potential difference between cerium sulfate (IV) and stannous chloride is considerably greater than that between cerium sulfate (IV) and arsenite. Arsenite is only titrated on heating the solution to 90°.

In order to determine $SnCl_2$ and Na_3AsO_3 when they are present side by side in the solution to be titrated, a small piece of marble is introduced into the solution and cerium sulfate (IV) is added dropwise until a shadow falls on the luminescent screen. The mixture is then heated to 90°, and cerium sulfate (IV) again is added until a second shadow appears. The number of mls of cerium sulfate (IV) used to titrate to the first end point corresponds to the amount of $SnCl_2$ in solution, while the number of mls of cerium sulfate used to get the second end point corresponds to the amount of arsenite. Titration results are given in Table 5.

TABLE 5

Sn taken, in mg	Sn found, in mg	Error, in mg	As taken, in mg	As found, in mg	Error, in mg
28.766	28.732	− 0.034	16.094	16.074	− 0.020
28.766	28.734	− 0.032	16.094	16.072	− 0.022

These results show that the accuracy of the determination of tin and arsenic when present together is the same as when they are determined independently.

Titration of Sulfite with Cerium Sulfate

Sulfites are normally determined in the visible spectrum iodometrically. The same drawbacks apply in this case as in the iodometric determination of tin. The errors are eliminated on using ultra-violet titration.

TABLE 6

SO_3^{2-} taken, in mg	SO_3^{2-} found, in mg	Error, in mg
17.962	17.972	+ 0.010
17.962	17.970	+ 0.008

Cerium sulfate (IV) can react with sulfite in two ways [10]:

1. $2Ce(SO_4)_2 + Na_2SO_3 + H_2O = Ce_2(SO_4)_3 + Na_2SO_4 + H_2SO_4.$
2. $2Ce(SO_4)_2 + 2Na_2SO_3 = Ce_2(SO_4)_3 + Na_2SO_4 + Na_2S_2O_6.$

On carrying out some tests, it became clear that in order to titrate sulfite completely, an amount of cerium is required which corresponds to the sum of these two reactions:

$$4Ce(SO_4)_2 + 3Na_2SO_3 + H_2O = 2Ce_2(SO_4)_3 + 2Na_2SO_4 + Na_2S_2O_6 + H_2SO_4.$$

In this case 1 ml of 0.1 N cerium sulfate corresponds to 0.050089 g of sulfite.

The end point, as in previous examples, is established by the appearance of shadow on the luminescent screen. During titration a small piece of marble is placed in the solution in order to avoid atmospheric oxidation. Results are given in Table 6.

Titration of Thiosulfate with Cerium Sulfate (IV)

When a solution of cerium sulfate (IV) is added rapidly to thiosulfate, the reaction which proceeds as follows occurs:

$$2Ce(SO_4)_2 + 2Na_2S_2O_3 + H_2SO_4 = Ce_2(SO_4)_3 + 2Na_2SO_4 + 3SO_2 + H_2S.$$

The end point is established by means of potassium iodide which acts as an ultra-violet indicator for the titration. Determination is carried out as follows: To the solution to be titrated is added 2-3 drops of 5% potassium iodide and titration carried out rapidly with cerium sulfate (IV) until the ultra-violet "color" of free iodine appears at the equivalence point. Titration results are given in Table 7.

TABLE 7

$S_2O_3^{2-}$ taken, in mg	$S_2O_3^{2-}$ found, in mg	Error, in mg
52.390	52.400	+ 0.010
52.390	52.395	+ 0.005

TABLE 8

Ce taken, in mg	Ce found, in mg	Error, in mg
135.010	133.600	+ 1.410
135.010	134.100	- 0.910

Titration can be carried out in reverse – cerium sulfate (IV) with thiosulfate. In this case potassium iodide is added to the solution of cerium sulfate to be titrated until all the iodine which separates out has dissolved completely, and the titration carried out with thiosulfate. In this case the error of determination increases somewhat because of the volatility of iodine (Table 8).

Titration of Potassium Thiocyanate with Cerium Sulfate (IV)

Potassium thiocyanate reacts with cerium sulfate (IV) according to the following equation:

$$6Ce(SO_4)_2 + KSCN + 4H_2O = 3Ce_2(SO_4)_3 + KCN + 4H_2SO_4.$$

The indicator for this titration in the ultra-violet, as before, is absorption of the ultra-violet by cerium sulfate (IV). Potassium thiocyanate does not absorb the ultra-violet at the operating wave length [11]. Titration is carried out as already described. Results are given in Table 9.

TABLE 9

SCN^- taken, in mg	SCN^- found, in mg	Error, in mg
2.397	2.390	– 0.007
2.397	2.387	– 0.010

Titration of Iodides with Cerium Sulfate

Willard and Young [2] established by potentiometric titration that the reaction between cerium sulfate (IV) and iodide quantitatively follows the equation:

$$2Ce(SO_4)_2 + 2KI = Ce_2(SO_4)_3 + I_2 + K_2SO_4.$$

We used this process for iodide determination in the ultra-violet. To the solution of potassium iodide to be titrated is added excess cerium sulfate (IV) until the iodide is completely oxidized, then 5-10 ml of 30% ammonium fluoride are added to combine with residual cerium sulfate (IV). The iodine is then titrated with thiosulfate to complete disappearance of the shadow on the fluor-

escent screen.[1] Results are given in Table 10.

TABLE 10

I taken, in mg	I found, in mg	Error, in mg
13.327	13.290	− 0.037
13.327	13.385	+ 0.058

TABLE 11

Pb taken, in mg	Pb found, in mg	Error, in mg
102.740	102.730	− 0.010
98.200	98.185	− 0.015

Titration of Solutions of Salts of Strontium, Calcium, Cadmium, Silver, and Lead with Cerium Sulfate (IV).

Because ions of strontium, calcium, cadmium, silver and lead do not act as reducing agents and do not react directly with Ce^{IV} ions, we worked out an indirect method for the determination of the metals mentioned using cerium sulfate (IV). The procedure adopted was as follows: to the solution of the metal salt to be titrated was added a known excess of standard sodium oxalate. The precipitate formed was filtered off, and the residual oxalic acid determined in an aliquot of the filtrate by titration with cerium sulfate (IV) in the ultraviolet using the method described above. The amount of metallic ion is then calculated by means of the following equations:

$$Me + C_2O_4^{2-} = \downarrow MeC_2O_4;$$
$$2Ce^{IV} + C_2O_4^{2-} = 2Ce^{III} + 2CO_2.$$

The mean experimental error for all the metals mentioned above does not exceed ±0.015 mg. Examples of results obtained with lead are adduced in Table 11.

ANALYSES OF LEAD ALLOYS

In order to check this cerimetric method in the ultra-violet, we used two alloys of the "Pripoi" type. A semi-quantitative spectrographic analysis was first made of the alloys in order to verify whether there are any elements present which may interfere with lead and tin determinations. As can be seen from the analytical results (Table 12), the elements which are present are present in amounts which will not interfere with the determination of tin and lead.

TABLE 12

Element	Alloy I	Alloy II	Element	Alloy I	Alloy II
	Amount in %			Amount in %	
Pb	Very high	Very high	Mg	0.001	0.001
Sn	−	Very high	Ca	−	0.001
Bi	0.01	0.01	Fe	0.01	0.001
Sb	−	0.01	Ni	−	0.001
Ag	0.001	0.01	Cu	0.01	0.001
Si	0.0001	0.0001			

Analysis of Alloy I

Determination of Lead. Results of gravimetric determination of lead by Dymov's method [12] are given in Table 13.

[1]) In view of the fact that on addition of ammonium fluoride to combine with excess cerium (IV), a precipitate of cerium fluoride is formed, it is recommended that a minimal excess of cerium be used.

Method of Determination in the Ultra-Violet. Ca. 0.1 g of alloy was dissolved in 15 ml nitric acid (1:1). The solution was diluted with water to 100 ml and neutralized to the methyl orange end point. To the neutral solution was added a drop of 78% acetic acid to get rid of turbidity. The solution was then evaporated to 10-15 ml and excess oxalic acid added. Residual oxalic acid was determined in the filtrate by titration with cerium sulfate (IV) and the amount of lead calculated from the results. Results are given in Table 14.

TABLE 13

Weight of $PbSO_4$, in g	Weight of Pb, in g	Pb, in %
0.1429	0.09779	97.79
0.1432	0.09783	97.83

TABLE 14

Aliquot, in g	Weight of Pb found, in g	Pb, in %
0.1000	0.09822	98.22
0.1000	0.09803	98.03

Analysis of Alloy II

1) Determination of Tin. Tin was determined first gravimetrically by Dymov's method [12]. Results are given in Table 15.

These results are in good agreement with those obtained by cerimetric titration of tin in the ultra-violet; the latter was carried out as follows: ca. 0.1 g of alloy was dissolved in 30 ml of concentrated hydrochloric acid. To the solution obtained were added small pieces of marble, and stannous chloride titrated with cerium sulfate (IV) in the ultra-violet. Results are given in Table 16.

TABLE 15

Weight of SnO_2, in g	Weight of Sn, in g	Sn, in %
0.2010	0.1583	31.66
0.2008	0.1576	31.52

TABLE 16

Aliquot, in g	Weight of Sn found, in g	Sn, in %
0.1000	0.03159	31.59
0.1000	0.03159	31.59

2) Determination of Lead. After precipitation of the metastannic acid, lead was determined in the residual filtrate both gravimetrically and volumetrically by the methods already described. Gravimetric and volumetric results are given in Table 17.

TABLE 17

Gravimetric Method			Volumetric Method		
Weight of $PbSO_4$, in g	Weight of Pb, in g	Pb, in %	Aliquot, in g	Weight of Pb found, in g	Pb, in %
0.09920	0.06773	67.73	0.1	0.06807	68.07
0.09940	0.06781	67.81	0.1	0.06813	68.13

These examples show that cerimetric determinations in the ultra-violet are just as accurate as the method normally used in the visible part of the spectrum.

G. Z. Ileva carried out some of the experimental work.

In conclusion I should like to thank Prof. Yu. V. Morachevsky for his continuous help in carrying out this work.

SUMMARY

1. The principles of cerimetric determination in the ultra-violet are described.

2. The limitations of the ultra-chemiscope for analytical purposes are discussed and a new apparatus is described by means of which titration can be

carried out in the ultra-violet.

3. Cerimetric determinations are described for antimony, tin, strontium, calcium, cadmium, silver and lead; a method is described for the cerimetric determination of tin and arsenic when they are present together.

4. Cerimetric methods are described for oxalates, sulfites, arsenites, thiosulfate, thiocyanates, and iodides.

5. The analysis of lead alloys by a cerimetric method in the ultra-violet is described.

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PHOTOCOLORIMETRIC DETERMINATION OF ANTIMONY IN ORES BY AN IODIDE-THIOUREA METHOD

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A method for the routine determination of antimony in ores which is convenient and rapid is that based on the formation of the greenish-yellow iodide-antimony complex. In order to deal with the iodine which is evolved during the formation of this complex, it is essential to add a reducing agent. Of a number of materials which we tested for this purpose, the most suitable proved to be thiourea; it differs from sulfurous acid and bivalent tin in that it does not form colored compounds in a sulfuric acid medium with either iodide or antimony.

In addition, thiourea eliminates interference from a number of other elements by combining with them to form colorless, soluble complexes [1-3]. This property has been used for the determination of antimony without preliminary removal of copper, iron, mercury, tin, and arsenic. In particular, the cuprous thiourea complex is so stable that even at molar concentrations of copper and iodide, no precipitate of cuprous iodide is formed if sufficient thiourea is present; nickel and cobalt do not interfere either as long as their amounts do not exceed 5-10 mg in 50 ml solution.

In addition to ions which interfere because of their characteristic color (large amounts of Ni^{2+}, Co^{2+}, Cr^{3+}), bismuth should also be completely absent, since, under the experimental conditions used, bismuth gives a colored complex whose color is 4 – 5 times more intense than the one formed by antimony.

The presence of more than 0.5% chloride leads to a weakening of the color because of the conversion of antimony to the colorless chloride complex. Nitrates and sulfates of the alkali metals, ammonium nitrate, and sulfate, as well as tartrates in the concentration range 0.2 – 2 N do not affect the optical density of the solution.

The very low stability of the iodide-antimony complex in aqueous media necessitates the use of a large excess of potassium iodide. Thus, in order to develop an initial color threshold (E = 0.01) at an antimony concentration of 0.0001 M, a 30-fold excess of iodide must be used, and on dilution of the solution to be determined colorimetrically 10 times, a 750-fold excess of iodide is necessary. The complex is more stable in diethyl ether media, by which it is readily extracted, but even in this case, not less than a 3-fold excess is necessary in comparison with the calculated amount required for formation of $HSbI_4$.

We used the following optimal reagent concentrations: 7.5 g H_2SO_4, 1.5 g KI and 0.1 g $CS(NH_2)_2$ in 50 ml solution.

The graphs in Figs. 1 and 2 show that the optical density of the solution increases with sulfuric acid and potassium iodide concentrations, but it does not increase steadily. A deviation of ± 15-20% in the acidity does not lead to significant changes in optical density; the complex behaves similarly in nitric acid. At the concentration of sulfuric acid employed, up to 0.4 N nitric acid can be present. With deviations of ±10% in the concentration of iodide employed from the accepted value, the optical density changes as follows: for 0.05 mg Sb by 9%, for 0.2 mg of Sb by 5%, and for 0.5 mg of Sb by 2%.

By working at high iodide concentrations and consequently at high thiourea concentrations, it is possible to increase the sensitivity 2 – 3 times, but even under the given conditions, it is possible to determine 0.002% Sb in aliquots of 0.5 g. The sensitivity is increased 10 times if the complex is measured colorimetrically in a diethyl ether medium or in a medium of another extracting solvent [4].

In increasing the thiourea concentration from 0.1 to 1 g in 50 ml, the optical density remains unchanged, but the stability of the complex with time decreases; in the presence of 0.1 – 0.2 g thiourea, the optical density is constant for 15 – 24 hours, but when 0.5 – 1 g of thiourea is present, the color beings to weaken after only 3 hours, and after 5 – 6 hours, turbidity as a result of sulfur separation appears – the sulfur is an oxidation product of thiourea.

When more than 20 mg of copper or iron is present, it is necessary to increase the thiourea content 2 – 3 times.

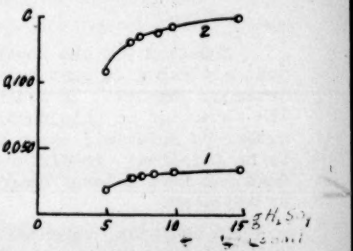

Fig. 1. The relation between optical density of solutions and the concentration of sulfuric acid: 1 - 0.05 mg in 50 ml; 2 - 0.2 mg in 50 ml.

Fig. 3 shows that the color of the complex follows Beer's law only in a narrow range of optical densities, predominantly at low antimony concentrations when the concentration of excess iodide is practically constant. The molar extinction coefficient (with a blue filter) is 1620 for a content of 0.02 mg; 1318 for 0.2 mg, and 533 for 2.0 mg of antimony in 50 ml of solution.

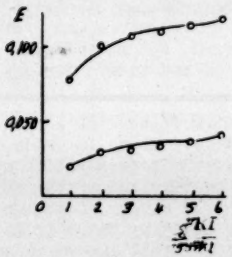

Fig. 2. Relation between optical density of the solutions and potassium iodide concentration: lower curve - 0.05 mg in 50 ml; upper curve - 0.2 mg in 50 ml.

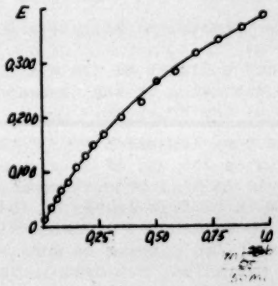

Fig. 3. Calibration curve. 30 mm cuvette, blue filter (400 – 450 mμ).

In order to decompose the ore and simultaneously remove antimony from interfering elements, it is expedient to use a method of sulfurization based on fusion with a mixture of sodium carbonate and sulfur [5, 6]. Thio- salts of antimony, arsenic, and tin, and also the thio- salts of any copper and mercury which may be present. Iron as a sol may also pass through the filter. All these interfering elements are masked by thiourea.

Bismuth is retained on the filter as a precipitate, whatever its relative amount with respect to antimony.

The polysulfides are broken down and the test solution made ready for colorimetric determination by treating the filtrate with a mixture of sulfuric and nitric acids with hydrogen peroxide, and subsequent evaporation of the solution until most of the sulfuric acid has been removed. By dissolving the salt residue in the presence of sulfuric acid, the danger of losing antimony by hydrolysis is removed. This can be carried out for contents of up to 6 mg of antimony in the test.

It is of interest to note a fact which we observed several times; viz., that for antimony contents no greater than 0.5 mg, the weakly acid salt residue can be dissolved in hot water alone and filtered without loss. Our experiments showed that an appreciable sodium sulfate concentration favors the stability of antimony sulfate to hydrolysis in the given case. The presence of iron and ammonium sulfates, on the other hand, favors hydrolysis.

The method was checked on ores, synthetic mixtures, and standard metal and alloy samples (tablets). The latter were dissolved in acids; antimony was precipitated with ammonia, using ferric hydroxide as a collector and was then subsequently determined as described below.

The relative experimental error for a content of up to 0.1% antimony varies within the limits 3 – 10%; for higher antimony concentrations, the error does not exceed 5%.

Maximum light absorption by the iodide-antimony complex occurs in the ultraviolet; for small amounts of antimony, therefore, a violet light filter is best (410 $m\mu$).

REAGENTS USED

1. Sintering mixture. Finely ground anhydrous sodium carbonate and stick sulfur, mixed in the ratio 4:3.

2. Sulfuric acid (1.42) (470 g/liter).

3. Solution for polysulfide oxidation. Two volumes of sulfuric acid (1.42) (470 g/liter) are mixed with one volume of hydrogen peroxide. The mixture is kept in a cool, dark place.

4. Sulfuric acid, 1.84.

5. Nitric acid, 1.4.

6. Potassium iodide-thiourea solution. 10 g thiourea and 150 g potassium iodide are dissolved in water in a 1-liter standard flask and made up to the mark. The solution keeps for 2 weeks.

7. Sodium sulfate, 1% freshly prepared solution.

8. Standard antimony solutions: 0.5 g and 0.1 g of antimony are dissolved with heating in 20 ml of 1.84 sulfuric acid. The cooled solutions are transferred to 1-liter standard flasks, and 1.42 sulfuric acid added to bring the volume up to the mark.

The two solutions thus prepared contain 0.5 mg/ml of antimony (A), and 0.1 mg/ml of antimony (B). By diluting solution B five times with 1.42 sulfuric acid, solution (C) with a concentration of 0.02 mg/ml antimony is prepared.

ANALYTICAL PROCEDURE

0.1 – 0.5 g of finely ground ore is mixed in a No. 2 porcelain crucible with 6 times its weight of sintering mixture and the charge covered with another 0.3 g of the same mixture. The crucible plus lid is placed either in a cold

muffle or one not hotter than 150° and gradually heated up to 300°; this temperature is maintained for 20 minutes. At this stage formation of polysulfides occurs and the excess sulfur burns. The temperature is then increased to 400-450° and kept here again for 20 – 30 minutes. During this second stage, the oxide and sulfide compounds of antimony are converted into sulfo salts. Higher temperatures must not be used; otherwise partial decomposition of the sulfo salts occurs.

The crucible is cooled and placed in a 100 ml beaker, 15 ml of water is added, and the whole taken up to the boil. The sintered mass is detached from the crucible and leached out. The glaze of the porcelain should be undamaged. The crucible is washed, and the washings filtered into another 100 ml beaker. The precipitate on the filter is washed 2 – 3 times with sodium sulfite solution. The precipitate containing the sulfides of Group 3 and 4 cations and the silica residue can be used for the determination of bismuth. The filtrate is usually colored golden-yellow or yellowish-brown, but it is sometimes greenish as the result of the presence of small amounts of iron sulfide; this, however, does not interfere with antimony determination.

Six to eight ml of the solution for oxidation of polysulfides is added. When this is done, sulfur should be precipitated as well as Group 5 sulfides. The solution is evaporated to a volume of 5 – 8 ml, 3 ml of nitric acid is added, and then evaporation is continued until white fumes of SO_3 appear. In the presence of nitric acid, the sulfur collects together into a lump which it is easy to filter. The inside of the beaker is washed down, and evaporation continued until the sulfur trioxide fumes begin to thin out, after which the beaker is removed from the heating source. If the amount of antimony is high (>1%), a point which it is easy to check on from the orange color of the precipitate after decomposition of the sulfo-salts, then evaporation is stopped at the stage when copious SO_3 fumes are being given off, and the salt residue forms a syrupy liquid (on cooling). The same procedure should be adopted when there is a considerable amount of tin in the ore. To the salt mixture obtained 5 ml of 1.42 sulfuric acid is added, and the mixture heated until complete solution is effected when 15 ml of hot water is added; the solution is mixed and filtered through a d = 5 cm filter into a 50 ml standard flask. Beaker and filter are washed with a small amount of water, another 5 ml of 1.42 sulfuric acid is added, and exactly 10 ml of the thiourea-potassium iodide solution, and the whole made up to the mark with water.

Color develops in one minute. The color is measured the same day; the blank which is used is carried through all the analytical stages.

If an FEK-M apparatus is used, one should take an SS-8 filter and a 30 mm long cuvette for amounts of antimony between 0.01 – 1 mg, and a 10 mm long cuvette for amounts of antimony between 1 – 6 mg.

Calibration curves (tables) are built up by means of standard solutions of antimony and reagents. The total volume of standard solution and sulfuric acid 1.42 should amount to 10 ml; tenths of a milliliter need not be taken into account. The blank should be one made up from reagents only. Visual colorimetric determination can also be carried out; this is best done by means of a standard scale in flat bottomed, 35 mm diameter cylinders. Color intensity is measured along the vertical axis of the cylinder against a white background.

The method described is applicable to ores of varying composition containing up to 3% of antimony, on an aliquot of 0.1 g. Forty to fifty analyses could be carried out in 2 days by one analyst.

TABLE

Results of Antimony Determinations in Synthetic Mixtures and Standard Samples

Amount of Sb taken in mg	Amount of Sb found in mg
0.05	0.045; 0.050; 0.050
0.20	0.20; 0.19; 0.19
2.0	1.99; 1.99; 1.96
0.20 + 10 mg Cu + 10 mg Sn + 10 mg As	0.20; 0.19
0.05 + 0.5 mg Hg + 5 mg Fe	0.05; 0.045
0.5 g ore	0.085
" " " + 0.1 mg Sb	0.18; 0.18
" " " + 0.1 mg Sb + 1 mg Bi	0.18; 0.18
2 mg Bi without antimony	0.00
" " " + 0.2 mg Sb	0.20; 0.19; 0.20
" " " + 0.05 mg Sb	0.045; 0.045; 0.050
0.2 g sample of ore	0.25; 0.24
" " " " " + 40 mg Cu + 20 mg Fe + 10 mg Bi	0.24; 0.23; 0.24
S.O. 91 nickel (~0.01% Sb)	0.014; 0.014%
S.O. 143 brass (<0.002% Sb)	0.001; 0.001%
S.O. 89 bronze (0.25% Sb)	0.25; 0.25; 0.27; 0.25%

SUMMARY

1. The use of thiourea as a reducing agent and complexing agent makes the colorimetric determination of antimony by means of the iodide-antimony complex method more accurate and selective. Using this method it is possible to determine antimony in the presence of copper, iron, tin, arsenic, and mercury.

2. The effect of reagent concentrations, other elements, and other factors on the optical density of the solutions has been studied. Optimal conditions for the photocolorimetric determination of antimony have been established.

3. By sintering the test sample with sodium carbonate and sulfur at 400 – 450°, followed by decomposition of the sulfo salts formed, the antimony can be separated from interfering elements and its determination in a large number of ore samples of varying composition speeded up.

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A NEW MICRO METHOD FOR THE DETERMINATION OF ANTIMONY AND ITS QUANTITATIVE SEPARATION AS STIBINE

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One of the properties which arsenic and antimony have in common is the capacity of their compounds to be reduced in acid media by nascent hydrogen to arsine and stibine respectively.

It is known, however, [1,2] that while trivalent arsenic in acid media is quantitatively reduced to arsine, no success has hitherto been recorded of the quantitative reduction of antimony to stibine. The difficulty of reducing antimony can be explained by the instability of stibine, which is easily oxidized to elemental antimony, which is then lost to determination. In addition, antimony (III) is more easily precipitated than arsenic (III) on the more electro-negative metals (zinc, iron, aluminum, cadmium, etc.), and thus when these react with acid, antimony does not participate in the reduction reaction to give stibine.

As a result the reduction of antimony (III) to stibine requires special conditions which do not include the reaction indicated above. In the literature [3] it is usually pointed out that micro amounts of antimony (III) are reduced to stibine under the same conditions as for conversion of arsenic to arsine.

Sanger and others [5,6] recommend that micro amounts of antimony (III) be reduced by nascent hydrogen obtained by the interaction of hydrochloric acid and zinc or by electrolysis with a lead cathode over which a stream of hydrogen is passed. In this last method, reduction of antimony (III) to stibine must be carried out in a large excess of hydrogen introduced from outside. We have been unable to find results re the quantitative reduction of antimony (III) to stibine.

In most investigations it is almost invariably necessary to combine quantitative determination with qualitative reactions (e.g., determination of micro amounts of antimony in biological material); it is most convenient to carry out the reactions for antimony after its reduction to stibine.[1] Stibine obtained as the result of the reduction reaction is very reactive and enters into many volumetric and oxidation-reduction reactions (with elemental iodine, silver nitrate and mercuric chloride or bromide, etc.). These reactions are also used for the determination of antimony after its reduction to stibine.

In the present paper we have described a new iodo-thiourea method for the determination of antimony, the conditions for carrying out the method, and the extent of the reduction of micro amounts of antimony (up to 5 mg) with nascent hydrogen:

$$SbO_2^- + 3Zn + 7H^+ \rightarrow H_3Sb + 3Zn^{2+} + 2H_2O.$$

---

[1]) E. B. Sandel points out [4] that the method of determining micro amounts of antimony (III) after reduction to stibine has not been worked out fully enough. Methods for determining antimony have usually a colorimetric finish based on the formation of a yellow color on paper soaked with mercuric chloride or bromide. These methods are difficult to carry out and give low results because small amounts of stibine do not give colors with paper soaked in the mercuric salts mentioned [7]. This is a drawback of Sanger's colorimetric method.

The stibine formed reacts in a glass tube with elemental iodine to give a non-volatile orange yellow antimony tri-iodide.

$$H_3Sb + 3I_2 \rightarrow SbI_3 + 3HI$$

which collects as one or two rings on the tube walls. This can be used as a qualitative reaction for antimony ions.

The antimony tri-iodide in the presence of potassium iodide is washed into a tartaric acid solution. In this solution iodine is reduced with ascorbic acid, while the antimony is easily converted into antimonyl tartrate by heating the solution.

Determination of antimony (III) in the solution obtained is based on the capacity of organic bases to give difficultly soluble colored double iodides $[R \cdot H]SbI_4$ (R – organic base). This reaction is used for the colorimetric determination of antimony. Thiourea was chosen instead of pyridine, the base described in the literature [3]; the advantage of thiourea as compared with pyridine is the greater stability of the thiourea iodide complex with antimony.

EXPERIMENTAL

Colorimetric Determination of Antimony by the Iodide-Thiourea Method

Before applying the iodide-thiourea method, it was essential to get accurate and reproducible results for antimony determinations in solutions of known antimony concentrations.

Determinations were carried out as follows: 0.5 ml of 20% potassium iodide solution containing 0.1% ascorbic acid was introduced into a 30 ml test tube and 0.5 ml of 8% thiourea and 10-15 ml of 8 N sulfuric acid added; finally 1-5 ml of antimony test solution was added. After thorough mixing, the color obtained was compared with a standard color prepared in the same way but for which a standard antimony solution was measured out accurately from a micro-buret, until the colors in the tubes matched. The final volumes were levelled with 8 N sulfuric acid (colorimetric titration method).

There was no need to use gelatin or gum arabic as protective colloids.

As a preliminary, we studied the stability at ordinary temperatures of the iodide-antimony complexes formed with various organic bases: pyridine, β-picoline, urotropine, urea, and thiourea. Two drops of starch solution were added to the test solution for control. Darkening of the solution in the course of a definite time interval (minutes, hours, days) indicated decomposition of the complexes.

The results obtained are given in Table 1.

These results show that the iodide antimony complexes formed with pyridine, β-picoline, urotropine and urea were only stable 10-20 minutes; the stability of these complexes with thiourea is better; these complexes do not break down within 24 hours.

In order to check on the methods which we have put forward, several determinations of antimony were made in solutions of known concentration. The results of these experiments are given in Table 2.

These results indicate that antimony can be determined fairly accurately and with good reproducibility.

In determining antimony with thiourea, the following conditions must be observed: a) equal volumes of thiourea and potassium iodide must be added to both standard solutions and the solutions to be determined colorimetrically. A proportional decrease in the stipulated amounts of reagents used in the standard and test solutions is permissible for very small concentrations of antimony in the test solution. Thiourea, in amounts greater than that indicated, weakens the color slightly, while smaller amounts of thiourea than that stipulated lead to instability of the color.

TABLE 1

Stability of Iodide-Antimony Complexes
Formed with Organic Bases

Base	Stability									
	10 min.	20 min.	30 min.	40 min.	60 min.	1.5 hrs.	2 hrs.	6 hrs.	12 hrs.	24 hrs.
Pyridine	+ −	−	−	−	−	−	−	−	−	−
β-Picoline	+ −	−	−	−	−	−	−	−	−	−
Urotropine	+	+ −	−	−	−	−	−	−	−	−
Urea	+ −	−	−	−	−	−	−	−	−	−
Thiourea	+	+	+	+	+	+	+	+	+	+ −

Notes. (+) is the time in the course of which the complex is stable; (+ −) is the time at the end of which the complex decomposes; (−) after the expiration of this time, the complex is broken down.

TABLE 2

Results of Antimony Determinations
by the Iodide-Thiourea Method

Amount of antimony taken, in mg	Antimony found, in mg	% Antimony found
0.002	0.002; 0.002	100.0
0.003	0.003; 0.003	100.0
0.005	0.005; 0.005	100.0
0.008	0.008; 0.008	100.0
0.010	0.010; 0.009; 0.010	97.0
0.050	0.048; 0.050; 0.050	98.6
0.100	0.102; 0.100; 0.100	100.7
0.250	0.247; 0.249; 0.250	99.0
0.500	0.502; 0.504; 0.495	100.0
1.000	1.000; 0.990; 0.992	99.4
3.000	3.006; 2.990; 2.990	99.8
5.000	5.020; 5.010; 5.000	100.2

b) The optimal acidity of the test and standard solutions when made up to the final volume should be equal to or greater than 6 N.

c) Oxidizing agents should be absent (nitrogen oxides, etc.); antimony used for determination should be either tri- or quinquevalent; quinquevalent antimony in the presence of HI is reduced to the tri form; mercury, bismuth, lead, copper, iron and excessive amounts of arsenic and tin should be absent.

d) The absolute amount of antimony in the aliquot to be determined should not exceed 200 − 250 μg and should not be less than 2 μg.

Liberating and Fixing the Stibine

The extent of the reduction of antimony (III) to stibine was studied when the hydrogen evolved was produced by the following reactions:

1) 4 M sulfuric acid and zinc;
2) 4 M sulfuric acid and aluminum;
3) 4 M sulfuric acid and "coppered" zinc.
4) 4 M sulfuric acid plus "coppered" zinc plus stannous chloride.
5) 4 M sulfuric acid, zinc, and potassium bromide.
6) concentrated hydrochloric acid (37%) and zinc.
7) concentrated hydrochloric acid (37%) and amalgamated zinc.

Tests were made as follows.

Apparatus for liberating and fixing H_3Sb

The test solution of antimony (III), 15 ml of acid and 6-8 g zinc [or as the case may be, 2-3 g aluminum, 2 ml of 20% potassium bromide, and 1 ml 20% stannous chloride(II)] were placed in a 30 ml test tube (see diagram). The test tube was fitted with a ground glass test tube to which was sealed a tube which served as a receiver for the stibine. This receiver should be 0.6-0.8 cm diameter and 10-12 cm long. Inside this tube was fixed 0.5-0.6 g of cotton or glass wool strewn with ca. 80 mg of iodine crystals. The wool was given a preliminary wash with water and dried. The joint should preferably be a ground glass one, though a rubber bung may be used as a last resort. The stibine evolved passed into the receiver, where it was absorbed by the elemental iodine.

If any stibine is evolved, it reacts with the elemental iodine to give characteristic orange yellow color rings on the tube walls. Even as little as 2 μg of antimony, on reduction to stibine with concentrated hydrochloric acid and amalgamated zinc, gave an orange red ring of antimony iodide on tube walls of 0.4 cm diameter, while amounts of ca. 1 mg and more of antimony gave 2 – 3 rings.

From the number and size of orange yellow rings formed only in the lower parts of the receiving tube, the analyst can get an approximate idea of how much antimony has taken part in the reaction. This is an important point since it will be necessary in the later stages to know how much liquid to use for direct colorimetric determination of the antimony, and this will depend on the amount of antimony present.

Apart from visual observation (fixation of stibine in the lower part of the tube), the analyst can carry out reactions which indicate the quantitative absorption of H_3Sb by elemental iodine (reactions of Guzeit and others).

When the reaction between zinc and acid was complete, usually after 30-40 minutes, the reaction between amalgamated zinc and concentrated hydrochloric acid took at least 2 hours, the receiving tube was disconnected from the test tube; 0.25 ml of 20% potassium iodide was then introduced into the tube from above and the tube subsequently washed out a few times with hot water, also through the top. The wash liquor was collected in a 35-40 ml beaker containing 2-3 ml of 20% tartaric acid. During this operation about 8-10 ml of liquid was collected which should contain all the antimony which has been reduced to stibine and absorbed by elemental iodine. This liquid also contained the excess iodine which was removed by the careful addition of ascorbic acid dropwise; 1-2 drops of 0,1% ascorbic acid solution was finally added in excess. The final solution obtained was boiled for 2-3 minutes. When the amount of antimony was small, it was boiled until the volume was only 3-4 ml. When a yellow color appeared during boiling, 1-2 drops of 0.1% ascorbic acid solution was added. The solution was transferred quantitatively from the beaker to a 25-100 ml standard flask, cooled, and made up to the mark with 20% tartaric acid. When a fairly large amount of antimony was present, aliquots of 1-2 ml were taken from this solution for colorimetric determination. When the amounts of antimony were small, the whole original solution of 3-4 ml (i.e., solution before being made up to standard volume) was used for the determination. Results on the determination of antimony after reduction to H_3Sb with hydrogen formed by the interaction of H_2SO_4 and Zn are given in Table 3.

These results show that antimony can be determined after reduction in amounts equal to 25.0 – 56.0%. The remainder of the antimony is precipitated on the zinc, or on reduction is transformed into the elemental state. Amounts of antimony less than 15 μg were not determined by this method of reduction.

TABLE 3

Determination of Antimony after Reduction to H_3Sb with Hydrogen Evolved by Interaction of H_2SO_4 and Zn

Antimony taken, in mg	Antimony found, in mg	Difference	Antimony found, in %
3.000	0.920	2.080	30.7
2.000	0.730	1.270	36.5
1.500	0.608	0.892	40.5
1.000	0.250	0.750	25.0
0.800	0.410	0.390	51.2
0.500	0.280	0.220	56.0
0.250	0.140	0.110	56.0
0.100	0.051	0.049	51.0
0.050	0.022	0.028	44.0
0.020	0.009	0.011	45.0

In the next series of experiments, we substituted aluminum for zinc. On heating, aluminum reacted with sulfuric acid, but no stibine was evolved. Antimony in the form of a dull black, velvety layer precipitated on the aluminum. The following mixture was then tried for reducing antimony (III) to H_3Sb: sulfuric acid plus "coppered" zinc (i.e., zinc, covered with copper as a result of the reaction $Zn + CuSO_4$). Under these conditions H_3Sb was evolved in insignificant amounts. Antimony precipitated on the copper and zinc. A similar phenomenon was observed when sulfuric acid plus "coppered" zinc and stannous chloride (II) was used. Metallic zinc reduced the Sn^{2+} and $[SnCl_6]^{2-}$ ions to the metal. The latter separated out as a spongy bulky precipitate.

$$Sn^{2} + Zn \rightleftarrows Zn^{2+} + Sn;$$

$$[SnCl_6]^{2-} + 2Zn \rightleftarrows 2Zn^{2+} + Sn + 6Cl^{-}.$$

The hydrogen evolved by the reaction of zinc and acid can also be used up to reduce Sn^{2+} and $[SnCl_6]^{2-}$. Our experiments showed that practically no stibine is evolved in the system acid – zinc – stannous chloride (II).

In all these experiments not more than 10% of the antimony introduced could be determined by reduction to stibine. It became essential, therefore, to find other suitable conditions whereby antimony (III) could be quantitatively reduced to stibine. The evolution of H_3Sb by the reaction of sulfuric acid and zinc in the presence of potassium bromide and also of hydrochloric acid and zinc was studied. Under these conditions 50 to 90% of antimony (III) was reduced to stibine.

The conditions under which stibine was formed were accordingly changed again in further experiments. By reduction with nascent hydrogen, antimony (III) can be partially precipitated on metals which are in front of it in the EMF series. In order to prevent precipitation and also to slow down the reaction between metal and acid, amalgamated zinc was tried. The amalgamated zinc reacted slowly with acid, but the hydrogen on the mercury surface had a high over-voltage. Such hydrogen, it was proved, quantitatively reduced the antimony (III) to stibine. Only a small amount of hydrogen thus prepared was necessary for this quantitative reduction to stibine. Results for the determination of various amounts of antimony are given in Tables 4 and 5.

As we see from the data of Table 4, antimony can be quantitatively determined (with accuracy of $\pm$ 0.3%) after reduction to H_3Sb with hydrogen obtained by the interaction of hydrochloric acid and amalgamated zinc.

These results show the reproducibility of the method.

We established further that half of the hydrochloric acid can be substituted by 4 M sulfuric acid without affecting the results.

TABLE 4

Determination of Antimony (from 2 to 100 μg) after Reduction to H_3Sb with Hydrogen, Obtained by the Interaction of Hydrochloric Acid and Amalgamated Zinc

Antimony taken, in μg	Antimony found, in μg	Difference, in μg	Antimony found, in %
2.0	2.0; 1.9; 1.9	0.1	96.5
3.0	3.0; 2.8; 2.9	0.1	97.0
5.0	4.9; 4.9	0.1	98.0
8.0	7.8; 8.0	0.1	98.7
10.0	9.7	0.3	97.0
12.0	11.7	0.3	97.5
15.0	14.8	0.2	98.0
20.0	20.1	0.1	100.5
25.0	24.2	0.8	96.80
30.0	29.0	1.0	97.0
40.0	39.1	0.9	97.9
50.0	49.2	0.8	98.4
80.0	81.0	1.0	101.2
100.0	97.8	2.2	97.8

TABLE 5

Determination of Antimony (from 100 μg to 5 mg) after Reduction to H_3Sb with Hydrogen, Obtained by the Interaction of Hydrochloric Acid and Amalgamated Zinc

Antimony taken, in mg	Antimony found, in mg	Difference, in mg	Antimony found, in %
0.100	0.097	0.003	97.0
0.200	0.197	0.003	98.3
0.400	0.392	0.008	98.0
0.500	0.488	0.012	97.6
0.800	0.788	0.022	98.5
1.000	0.978	0.022	97.8
2.000	2.010	0.010	100.5
3.000	2.980	0.020	99.3
4.000	4.030	0.030	100.7
5.000	5.000	0.000	100.0

Conditions for the Quantitative Reduction of Antimony (III) to Stibine during the Reaction of Amalgamated Zinc with Hydrochloric Acid

a) Antimony is more easily reduced to stibine and also to elemental antimony than arsenic; e.g., when the reduction reaction is very vigorous, some of the antimony is converted into the elmental stage and is, therefore, not available for conversion to stibine. Consequently, hydrogen evolution by the action of hydrochloric acid and amalgamated zinc should not be too vigorous. The reaction should proceed slowly and smoothly without any sudden surges and frothing. The volume of liquid should not increase appreciably as the result of hydrogen evolution. If the amalgamated zinc is properly prepared, this condition will be observed.

b) The hydrochloric acid used for reacting with amalgamated zinc should be at least 9 M (ca. 30%).

c) Reduction of antimony (III) to stibine should be effected at 15 to 20°; the apparatus is immersed in cold water if overheating occurs.

d) Reduction of antimony (III) to stibine should take not less than 2 hours.

e) During the reduction to stibine, reducing agents (HI, HBr) and also copper, tin, aluminum, or their ions should be absent.

I should like to thank I. P. Alimarin for his help in writing this article.

SUMMARY

1. A new method for the colorimetric determination of antimony (III) with thiourea is proposed. The advantages of this method as compared with the pyridine-iodide method is the stability of the iodide-antimony complex over a period of 24 hours.

2. Optimal conditions are given for the quantitative reduction of antimony (III) to stibine by the reaction of amalgamated zinc with concentrated hydrochloric acid. Results with good reproducibility are obtained with an error of ± 3.0%.

3. The stibine evolved by the procedure outlined is quantitatively absorbed in a receiving tube containing elemental iodine, and the antimony is subsequently converted into antimonyl tartrate.

4. In the course of the quantitative determination of antimony, a reaction is employed by means of which antimony can be detected qualitatively by the formation of orange yellow antimony iodide. The reaction is specific; its limiting sensitivity is 2 μg antimony.

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DETERMINATION OF ACRYLONITRILE BY A CYANO-ETHYLATION REACTION

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Acrylonitrile $CH_2=CH-CN$ is produced and used on a large scale for the preparation of synthetic rubber and plastics, so that methods for its analysis are of practical importance. Since the qualitative composition of mixtures containing it may be rather varied, it is necessary to have various methods of determining acrylonitrile which are suitable for the various conditions under which it is found.

The physical methods which have been suggested for its determination – spectrophotometric [1], polarographic [2], and spectroscopic (infra-red) [3] – are not generally applicable; moreover they require special apparatus. Other methods which are simple by virtue of the use of a titration technique cannot be used for determination of acrylonitrile in colored solutions, because the end point itself is determined by a color change. One of these methods is based on the oxidation of the double bond in acrylonitrile with permanganate solution in the presence of sulfuric and hydriodic acids [4]. The error in this case is $\pm$ 5%.

A second method uses the reaction between acrylonitrile and dodecylmercaptan, the excess of which is titrated with iodine. The accuracy of this method is $\pm$0.22% [5]. It has been shown recently [6] that the simple volumetric titration of dodecylmercaptan with iodine can be replaced by potentiometric titration so that acrylonitrile can be determined in colored solutions.

The usual method of analyzing nitriles – alkaline saponification – in particular in the presence of hydrogen peroxide [7], and subsequent determination of the ammonia evolved, is not accurate enough in the case of acrylonitrile, and is not always practicable, since the nitrile groups of other compounds which accompany technical acrylonitrile are hydrolyzed under the same conditions (ethylenecyanohydrin, acrylonitrile polymers, etc.).

Research on the cyano-ethylation of α-amino acid derivatives [8] led us to develop a fairly simple method for the quantitative determination of acrylonitrile. α-Amino acids in the form of their alkali salts react easily with acrylonitrile in aqueous solution [9]:

$$NaOOC\underset{R}{C}HNH_2 + CH_2=CHCN \rightarrow NaOOC\underset{R}{C}HNHCH_2CH_2CN.$$

The new method proposed is based on a reaction which proceeds quantitatively between acrylonitrile and an aqueous solution of the potassium or sodium salt of glycine, the most readily available amino acid. To the aliquot of acrylonitrile a known amount of a solution of glycine of known concentration is added; on completion of the reaction, excess of the latter is determined gasometrically by Van Slyke's method, by means of which only amino acids containing the primary amino group are determined. This method is applicable in the case of colored solutions, and permits determination of acrylonitrile with an accuracy of $\pm$ 1% in mixtures containing ethylenecyanohydrin, water, and acrylonitrile polymers.

Van Slyke determinations are carried out in the usual apparatus [10]. We used a new micro apparatus which was made in the Protein Chemistry Laboratory of Moscow University by Ioanisiani [11]. The main feature of this apparatus is the use of an ordinary medicinal glass syringe as a reaction vessel of variable

volume, which simplifies, speeds up, and makes the determinations more accurate.

Conditions were chosen such that on the one hand possible side reactions, such as the saponification of acrylonitrile and dicyano-ethylation:

$$\underset{R}{NaOOCCHNH_2} + CH_2{=}CHCN \rightarrow \underset{R}{NaOOCCHN(CH_2CH_2CN)_2},$$

are excluded, while on the other hand, the reaction between glycine and acrylonitrile is quantitative. The conditions for analytical determination of acrylonitrile finally chosen were as follows: the amount of acrylonitrile in the aliquot to be analyzed should be ca. 0.1 g, while the molecular ratio of reagents should be glycine:acrylonitrile 2.5:1; solvent – water – 10 ml; reaction time, 1 hour; temperature – room. Attempts to lower the reagents ratio and to increase the total concentration in solution, and also cutting down reaction time by heating, all led to low results. Thus, on using the conditions given above but cutting down the time to 30 minutes, only 84.5% of the acrylonitrile reacted. Lower alcohols which complicate carrying out Van Slyke's gasometric determination of amino groups, interfere with acrylonitrile determination. Other compounds which can interfere are those which contain an active double bond of the acrylonitrile type (crotonitrile, acrylates) because they also react with glycine, as shown by preliminary experiments.

Results are given in the table for the analysis of pure acrylonitrile samples and of acrylonitrile in admixture with water and ethylenecyanohydrin:

Expt. No.	Aliquot taken in g	Composition of sample			Acrylonitrile found in %
		Acrylonitrile	Water	Ethylenecyanohydrin	
1	0.1047	100	–	–	99.8
2	0.1075	100	–	–	100.1
3	0.1127	100	–	–	100.2
4	0.1094	100	–	–	101.0
5	0.1123	96.7	–	3.3	96.8
	0.1009				96.9
6	0.1120	92.7	2.1	5.2	93.4
7	0.1075	91.1	1.4	7.5	91.6
	0.1273				92.3
8	0.2354	49.2	10.9	39.9	49.1
	0.2010				49.7
9	1.0432	10.1	30.2	59.7	9.5
	1.1102				9.9

EXPERIMENTAL

Reagents

1. Glycine solution. 38 g (ca. 0.5 M) of glycine is dissolved in water and 28 g (ca. 0.5 M) of potassium hydroxide and 1 g of sodium fluoride (for prevention of mold formation) added, and the whole diluted to 1 liter. The solution can be kept for a long time.

2. 30% solution of sodium nitrite.

3. Permanganate solution (50 g of potassium permanganate and 25 g of sodium hydroxide in 1 liter of water).

4. 50% potassium iodide.

5. 30% sodium hydroxide.

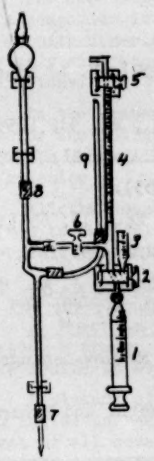
6. Glacial acetic acid.

7. Acrylonitrile dried over calcium chloride and twice distilled, boiling point 77 – 78° (760 mm) was used for standardizing the glycine solution.

Analytical Procedure and Apparatus

10 ml of the glycine solution is pipetted into a 50 ml conical flask fitted with ground glass stopper, and an aliquot of test material added (the amount of acrylonitrile in the aliquot should be ca. 0.1 g). The flask is shaken gently and allowed to stand stoppered for 1 hour at room temperature, after which it is neutralized with acetic acid (8-10 drops of glacial acetic acid) to a phenolphthalein end point (the neutralized solution can be kept for an indefinite time).

1 ml of 50% potassium iodide is next added[1]), and the solution is diluted to 100 ml with water in a standard flask. 1 ml of this solution is taken in order to determine amino nitrogen gasometrically in the Ioanisiani apparatus (see diagram).



Amino nitrogen is determined as follows: 1 ml of solution is introduced into funnel 3 by means of a pipet. Having passed it through tap 2 into the syringe, 1, 3 is washed with 1 ml of water, and this is also passed into the syringe. 5 ml of nitrous acid solution (prepared by shaking 1 ml glacial acetic acid with 4 ml 30% $NaNO_2$ solution in a 10 ml measuring cylinder) is next passed through funnel 3 into syringe 1. All these operations are carried out in such a way that when tap 2 is closed, the bore of the tap and also the bottom of funnel 3 are filled with liquid. Ca. 3 ml of 30% NaOH is placed in 3, and the syringe shaken for 3 minutes. When the reaction is complete, the alkali is allowed into the syringe, followed by small amounts of alkaline permanganate (4-5 ml), so that on shaking, the oxides of nitrogen are absorbed. When this is done, the syringe piston is moved upward. When alkaline permanganate is clearly visible around the bubble of gas which remains, 1-2 ml of water is carefully passed through funnel 3, and the nitrogen is carefully expelled through tap 2 into the buret by slight compression of the syringe piston. Having closed taps 2 and 3, tap 6 is opened, and with the aid of beads 7 and 8 the levels of water in tube 9 and buret 4 are equalized. When the gas volume has been measured, taps 2 and 5 are opened, and the mixture expelled by means of the piston. The system is washed with a solution of oxalic acid and twice with water.

Acrylonitrile content is determined by means of the formula:

$$\% \text{ acrylonitrile} = \frac{\text{mol. wt. acrylonitrile} \cdot 100}{S \text{ mol. wt. nitrogen} \cdot 10} (T - a) =$$

$$= \frac{53.06 \cdot 100}{S \cdot 140} (T - a) = \frac{37.9}{S} (T - a),$$

where S – is the weight of test mixture; a – the number of milligrams of nitrogen in the solution as determined gasometrically.

$T = \frac{T'}{10}$ (where T' is the number of milligrams of nitrogen in 1 ml of the glycine salt solution) is the standard titer; this is determined in a separate experiment in which pure acrylonitrile, assumed to be 100%, is used instead of the test mixture. T is given by the formula:

$$T = \frac{S_1}{0\ 379} + a_1,$$

1) KI is added in order to get constant results for the determination of glycine.

where S_1 . is the weight of pure acrylonitrile taken; a_1 – the number of milligrams of nitrogen in 1 ml of solution as determined gasometrically.

SUMMARY

A new method has been developed for the analysis of acrylonitrile, which is based on the reaction between the latter and glycine.

By means of this method, acrylonitrile can be determined in colored mixtures which contain water and ethylenecyanohydrin with an accuracy of up to ± 1%.

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ANALYSIS OF SILICO-ORGANIC COMPOUNDS

QUALITATIVE ANALYSIS OF MIXTURES OF ALKOXYSILANES WITH ALCOHOLS AND SILICON TETRACHLORIDE

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Despite the ever increasing use in industry of silico-organic compounds, their analysis has not been developed fully enough. The first qualitative reactions for silico-organic compounds were proposed by Soviet scientists [1-6].

The necessity of analytical methods and production control for silico-organic compounds is obvious, since during the production of these compounds, mixtures with other compounds are inevitably obtained, and the required compounds are only separated from these others in a more or less pure form by a series of operations.

In the present paper we describe a number of methods which we have worked out for the qualitative analysis of mixtures of certain alkoxysilanes with alcohols and silicon tetrafluoride, which are the compounds most often met with in practice

All the compounds which we used for making up synthetic mixtures were subjected to careful purification, and had the requisite physical constants. The inorganic reagents used were chemically pure or analytical grade.

Detection of $SiCl_4$ in Tetramethoxy- and Tetraethoxy Silanes

1. Reaction with Hydrogen Iodide or Potassium Iodide. We found that on heating hydrogen iodide with mixtures of ortho silicic acid esters and $SiCl_4$, free iodine is evolved. Pure $SiCl_4$ reacts in the same way even in the cold.

A mixture of 1-2 ml of test material and 2-3 drops of concentrated hydrogen iodide is heated in a test tube in a glycerol bath, the test tube being first of all covered with ashless filter paper soaked with saturated $Hg(NO_3)_2$ solution. Any $SiCl_4$ present will lead to a brown coloration of the paper. If the paper turns red this indicates the presence of the methyl or ethyl esters of ortho silicic acid [4], and the absence of $SiCl_4$.

Iodine is also evolved when $SiCl_4$ vapor reacts with potassium iodide.

The evolution of iodine by the action of $SiCl_4$ on HI or KI can be explained by the oxidizing properties of $SiCl_4$ [7].

$$2SiCl_4 + 2KI \longrightarrow Cl_3Si{-}SiCl_3 + 2KCl + I_2.$$

2. Reaction with Aniline or with an Aniline Solution of Tetramethyldiaminobenzophenone. In order to detect $SiCl_4$ in methoxy and ethoxysilanes, it is also possible to use the reaction with aniline or an aniline solution of tetramethyldiaminobenzophenone [2].

To 5-6 drops of test mixture is added 1-2 drops of aniline or an aniline solution of tetramethyldiaminobenzophenone. If $SiCl_4$ is present, then in the first instance a white precipitate appears, while in the second instance, a yellow precipitate is formed which is soluble in excess reagent.

3. Reaction with Water. It is also possible to detect $SiCl_4$ in methoxy and ethoxy silanes by the action of water. Hydrochloric acid is formed by the action of water on $SiCl_4$, and this can be detected with an indicator.

4-5 drops of test solution are placed in a small test tube, blue litmus paper is also introduced, and a few drops of water added rapidly. If $SiCl_4$ is present, a white gelatinous precipitate of silicic acid forms, while the litmus paper turns red.

4. Reaction with Potassium Bichromate and Nitric Acid. We found that potassium bichromate in dilute nitric acid gave a characteristic blue-violet color with methoxy and ethoxy silanes. If $SiCl_4$ is present, the rate of formation of this color is slowed down considerably.

To 5 ml of dilute nitric acid (1:2) contained in a test tube is added with cooling 5 drops of 5% potassium bichromate and 1-2 ml of test material, and the whole shaken up.

A blank is made simultaneously. In a test tube containing ester which contains $SiCl_4$, the blue color appears about 2-3 times slower than in esters which do not contain $SiCl_4$.

5. Reaction with Ferric Ferrithiocyanate. We found that the presence of $SiCl_4$ in tetramethoxy and tetraethoxy silanes leads to decolorization of $Fe[Fe(SCN)_6]$ solution.

A small lump of paper treated with an alcoholic solution of $Fe[Fe(SCN)_6]$ and 1-2 ml of CH_3OH is placed in a small test tube. The alcohol will be colored red by the $Fe[Fe(SCN)_6]$. 8-10 drops of test solution is then added; if $SiCl_4$ is present, the red color disappears.

Results of the analysis of mixtures of methoxy and ethoxy silanes with silicon tetrachloride are given in the Table.

Detection of CH_3OH in $(CH_3O)_4Si$ and of C_2H_5OH in $(C_2H_5O)_4Si$

1. Reaction with Metallic Sodium. In order to detect the corresponding alcohols of tetramethoxy and tetraethoxy silanes reaction with metallic sodium was used.

1-2 ml of test mixture was placed in a test tube and a lump of clean sodium, washed in absolute diethyl ether, added.

Any alcohol present in the test esters will lead to turbulent evolution of hydrogen and the formation of the corresponding alkoxides.

The reaction is very sensitive and less than 1% of alcohol can be detected.

2. Reaction with Ferric Ferrithiocyanate. We found that methoxy- and ethoxy silanes, in contrast to the respective alcohols, do not dissolve $Fe[Fe(SCN)_6]$. The reaction with $Fe[Fe(SCN)_6]$ can therefore be used for the detection of the alcohols in alkoxysilanes.

1-2 ml of test mixture and paper treated with an alcoholic solution of $Fe[Fe(SCN)_6]$ and dried, are placed in a test tube. If alcohol is present, the liquid will be colored rose or red. For mixtures of $(CH_3O)_4Si + CH_3OH$, the limit of identification is 0.65 mg CH_3OH, and the limiting concentration, 1.0%. For mixtures of $(C_2H_5O)_4Si + C_2H_5OH$ the limit of identification is 2 mg C_2H_5OH. Limiting concentration 1%.

3. Reaction with Silicon Tetrachloride. Reaction with $SiCl_4$ can also be used for the detection of methyl alcohol in methoxy silane.

1-2 ml of test material is placed in a test tube and a piece of blue litmus paper introduced. A few drops of absolutely dry $SiCl_4$ are added. The test tube is stoppered and shaken. If CH_3OH is present the litmus will turn red. Limits of identification, 6.5 mg. The limiting concentration is 5%. In order

TABLE

Result of the Analysis of Mixtures of Tetramethoxysilane and Tetraethoxysilane with Silicon Tetrachloride

Reagent	Indicator	Effect of reaction	Sensitivity, in mg $SiCl_4$	Limiting concentration $SiCl_4$, in %	Temperature °C
		Mixtures of $(CH_3O)_4Si$ + $SiCl_4$			
Hydrogen iodide	$Hg(NO_3)_2$ paper	Brown color	9.7	5	85-95
Potassium iodide	Starch paper + KI	Bluish brown color	6.5	10	70-75
Aniline	–	White precipitate	0.5	1	18-20
Aniline solution of tetramethyldiaminobenzophenone	–	Yellow or orange precipitate	0.5	1	18-20
Water	Blue litmus paper	Change of color of litmus to red + white precipitate	0.16	<1	18-20
Potassium bichromate and nitric acid	(Rate at which blue color appears is slowed down 2-3 times as compared with pure material)			10	18-20
$Fe[Fe(SCN)_6]$	Solution of $Fe[Fe(SCN)_6]$ in methanol	Decolorization of solution	1.3	1	18-20
		Mixtures of $(C_2H_5O)_4Si$ + $SiCl_4$			
Hydrogen iodide	$Hg(NO_3)_2$ paper	Brown color	13	19	110-120
Potassium iodide	Starch paper + KI	Bluish-brown color	6.5	10	70-75
Aniline	–	White precipitate	0.5	1	18-20
Aniline solution of tetramethyldiaminobenzophenone	–	Yellow or orange precipitate	0.65	1	18-20
Water	Blue litmus paper	Litmus paper turns red + white precipitate	0.16 1.2	<1	18-20
Potassium bichromate and nitric acid	(Rate at which blue color appears is slowed down 2-3 times as compared with pure material)			10	18-20
$Fe[Fe(SCN)_6]$	Solution of $Fe[Fe(SCN)_6]$ in methanol	Decolorization of solution	1.3	1	18-20

to detect C_2H_5OH in tetraethoxy silane, heating is necessary.

Detection of the Methyl and Ethyl Esters of Ortho Silicic Acid in the Presence of Alcohols or $SiCl_4$

If only $SiCl_4$ is present, methoxy and ethoxysilanes can be detected by the reaction with borax in the presence of hydrochloric or sulfuric acids [1, 4]. During this reaction methyl borate or ethyl borate are formed which color a burner flame green. Limit of identification for $(CH_3O)_4Si$, 10 mg, while for $(C_2H_5O)_4Si$ it is 20 mg.

If only the alcohols are present, the methoxy or ethoxy silanes can be detected by heating with hydrochloric acid [4]; during this reaction a precipitate of silicic acid is formed which can be colored with methylene blue. Limit of identification, 2 mg of the alkoxysilane.

SUMMARY

1. A scheme for the qualitative analysis of the following mixtures has been worked out: a) tetramethoxy silane and silicon tetrachloride; b) tetramethoxysilane and methyl alcohol; c) tetraethoxy silane and silicon tetrachloride; and d) tetraethoxysilane and ethyl alcohol.

2. Two new qualitative reactions have been found for silicon tetrachloride: a) formation of free iodine on interaction with hydrogen iodide or iodides; b) decolorization of an alcoholic solution of ferric ferrithiocyanate.

3. It has been found that tetramethoxy- and tetraethoxy silanes, in contrast to the corresponding alcohols, do not dissolve ferric ferrithiocyanate. On this basis, a method has been worked out for the qualitative determination of alcohols in alkoxysilanes.

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SPECIFIC ATOMIC GROUPINGS IN REAGENTS FOR TUNGSTATES

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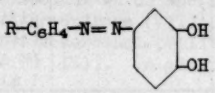
The outstanding research work of L. A. Chugaev [1, 2, 3], who discovered the reaction of α-dioximes with nickel and other ions, is the basis of the theory of specific atomic groupings. This theory has received its furthest development chiefly at the hands of Soviet scientists. In the course of the last 15 years specific atomic groupings have been discovered which determine the analytical reactions of organic compounds with Al^{3+}, Zr^{4+}, Hf^{4+}, Th^{4+}, V^{4+} – Kuznetsov [4,5,6,7,8]; Mg^{2+}, In^{3+} – Kulberg [9,10,11]; and BO_3^{3-} – Korenman [12], etc.

Organic reagents which have been suggested for the detection of tungstates are discussed in the present article, and it is shown that their activity is determined by a definite and specific atomic grouping.

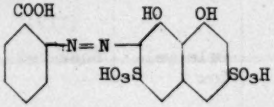
The number of atomic reagents suggested for the detection of tungstates is very limited. Kuznetsov [13], has studied the reactions of a number of azo dyes – pyrocatechol derivatives (I) with tungstates



(I)

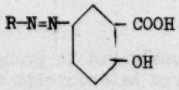
where R = NO_2; SO_3H; NH_2

Kuznetsov [14] suggested a reaction for the detection of WO_4^{2-} involving an azo dye of the composition

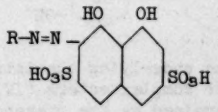


Schäfer [15] used a color reaction with curcumin for detection of WO_4^{2-}. Reactions with uric acid and phenols [16], α-benzoinoxime [17], and others [18, 19] have also been suggested.

During a study of the analytical reactions of azo dyes – salicyl derivatives (II), (19 reagents) and chromotropic acid (III) (10 reagents)



(II)



(III)

where R = C_6H_5; $C_6H_4NO_2$; $C_6H_4SO_3H$; $C_6H_4AsO_3H_2$; $C_6H_4N(CH_3)_2$, etc., we found [20] that under certain conditions of carrying out the reactions, color reactions were given with tungstates despite the considerable variation in reagent composition.

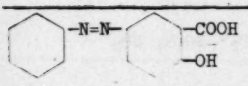
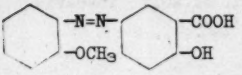
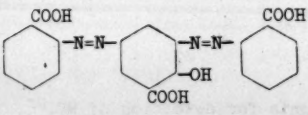
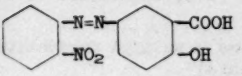
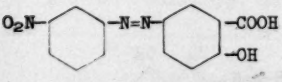
In carrying out these reactions, we used the method of comparison of test samples in the dry state [12]. Color reactions observed on the dry residues may be considered to be of the solid phase type described by Kuznetsov [21].

The reactions were carried out as follows: to 1-2 drops of 1% tungstate contained in a porcelain crucible were added 1 drop of reagent solution, 1-2 drops of a 2N sodium hydroxide, and 3-4 drops of 2N hydrochloric acid. The solutions were mixed and evaporated to dryness on a sand bath. The color of the dry residue was compared with a control

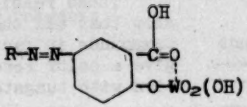
Results are given in Table 1 for five azo dyes – salicylic acid derivatives – which showed the highest sensitivity for tungstates.

TABLE 1

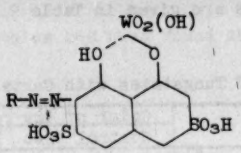
Reactions of Certain Azo Dyes – Derivatives of Salicylic Acid – with Tungstates

Reagent	Color of dry residue		Sensitivity	
	Control test	Test with WO_4^{2-}	Limit of identification, γW in 1 ml	Limiting concentration
	Pale rose-yellow	Bright orange-red	3	1:10000
	Pale yellow	Bright red	3	1:10000
	Pale yellow	Rose-red	6	1:5000
	Pale rose-yellow	Orange-red	30	1:1000
	Pale yellow	Orange-red	30	1:1000

The underlying chemistry of the reactions considered is probably the formation of inner complex esters (IV, V) with a six membered heterocyclic ring; the reaction is determined by the presence of a specific atomic grouping (VI), which is common to both chromotropic and salicylic acids



(IV)

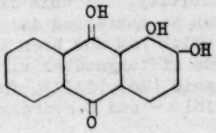


(V)

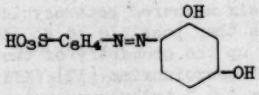
(VI)

where O* is the oxygen atom which forms a coordinate bond.

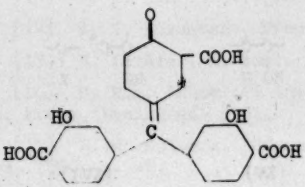
If this assumption is correct, then other organic compounds of different classes but containing this specific grouping should interact with tungstates. Among those compounds which contain this grouping, we tested: alizarin [1,2-dihydroxyanthraquinone (VII)], the azo dye, Tropeolin "O" [sodium salt of sulfobenzeneazoresorcinol (VIII)], and aluminon [ammonium salt of aurine tricarboxylic acid (IX)]. In addition the oxime [8-hydroxyquinoline (X)] was tested.



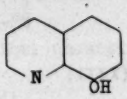
(VII)



(VIII)



(IX)



(X)

Results are given in Table 2.

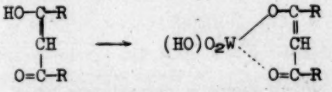
TABLE 2

Reactions of Tungstates with Certain Organic Compounds

Reagent	Color of dry residue	
	Control test	Test with WO_4^{2-}
Alizarin	Pale yellow	Yellow brown
Tropeolin "O"	Pale yellow	Greenish yellow
Aluminon	Rose	Bright orange-red
Oxime	Colorless	Yellow brown

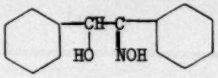
These results show that all these compounds in fact give a color reaction with tungstates.

This same atomic grouping enters into the composition of curcumin (XI), the chemistry of the reaction of which with tungstates has not been hitherto considered [15]. The chemistry of this reaction can now be explained on the basis of the viewpoint developed by us:



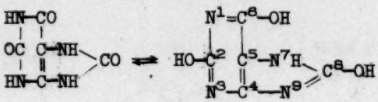
(XI) where R = CH=CH–$C_6H_3(OCH_3)OH$.

It is known from Korenman's work [22, 23] on the theory of specific atomic groupings that the oxygen atom which forms the coordinate bond can be replaced by a nitrogen atom. Moreover, one of the carbon atoms which make up the specific grouping can be removed without loss of reactivity. If this is taken into account, the six membered heterocyclic ring can be converted into a five membered ring. It is then possible to do something which has not been attempted before; viz., clear up the chemistry of the reactions of tungstates with pyrocatechol [13] (I), α-benzoinoxime [17] (XII), uric acid [16] (XIII), for which the tautomeric form – 2,6,8-trihydroxypurine, is possible – and 8-hydroxyquinoline.



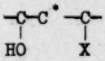
(XII)

(XIV)



(XIII)

(XV)

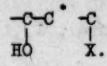


(XVI)

on the basis that the atomic groupings (XIV) and (XV) are special cases of a more general grouping (XVI), where X is the atom of oxygen or nitrogen forming the coordinate bond, and C* denotes the carbon atom, removal of which does not lead to loss of reactivity.

SUMMARY

1. A specific atomic grouping for tungstates has been found in some organic reagents –



The carbon atoms forming the group may occur in both aliphatic and cyclic compounds.

2. It has been shown that organic compounds of different classes containing the specific group indicated can give reactions with tungstates.

3. The underlying reaction is apparently the formation of five or six membered heterocyclic inner complex esters of tungstic acid.

4. The hypothesis developed explains the underlying chemistry of reactions which have been described previously between tungstates and curcumin, azo dyes – pyrocatechol derivatives, α-benzoinoxime, and uric acid.

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QUANTITATIVE DETERMINATION OF TIN WITH ARSONIC ACIDS

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Results of a study of the precipitation conditions of tin by aromatic arsenic compounds have shown that p-hydroxyphenylarsonic acid precipitates tin from acid solutions in the form of difficultly soluble tin p-hydroxyphenylarsonate [1]. This fact has served us as a basis for developing a volumetric method of determining tin. In recent years several papers have been published on the quantitative determination of tin by means of phenylarsonic acid. Knapper, Craig, and Chandlee [2] suggested phenylarsonic acid ass precipitant for Sn (IV). A series of papers followed in which the possibility of using this acid for the quantitative determination of tin was investigated. Of the papers devoted to this question, mention should be made of those of Syrkomsky and Pilnyak [3], Alimarin and Vezhenkova [4], and Kuznetsov [5]. In the last paper listed, Kuznetsov in considering the reasons for the contradictory results obtained by various authors for the determination of tin by means of phenylarsonic acid, came to the conclusion that during the precipitation of tin by means of this acid, it is essential to have the tin in the form of the chloride of metastannic acid since the behavior of the α- and β-compounds of Sn (IV) toward this acid is different. In examining this fact more closely the author exhaustively studied the gravimetric determination of tin by means of phenylarsonic acid.

None of these authors posed the problem of volumetric determination of tin.

We came up against this point during a study of the possible application of various arsonic acids in chemical analysis. Our main object was to develop more rapid analytical methods, and naturally we turned to volumetric methods.

As pointed out already during a study of precipitation conditions of various cations by phenylarsonic acid and some of its derivatives, it turned out that p-hydroxyphenylarsonic acid precipitates tin and certain other elements from mineral acid media. The overwhelming majority of cations are not precipitated under these conditions just as in the case with phenylarsonic acid itself.

Preliminary tests carried out in order to determine optimum precipitation conditions showed that at acid concentrations where most elements are not precipitated at all[1], tin is practically completely precipitated.

Precipitation of Quadrivalent Tin

A few drops of hydrogen peroxide are added to the test solution which contains ca. 0.001 g Sn per ml, and the solution heated for 10 minutes. On cooling, precipitation is effected by means of 5% sodium p-hydroxyphenylarsonate. The precipitant is added in a one and a half excess.

After addition of all the precipitant an equal volume of water is added and the whole heated for half an hour on a boiling water bath. After cooling the precipitate is filtered off and washed 2-3 times with water.

Analysis of the tin p-hydroxyphenylarsonate thus prepared indicated the following composition:

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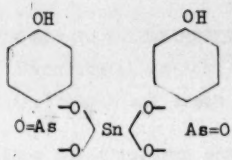
[1]) Salts of copper, zinc, and lead, etc., are not precipitated.



Method of Treating the Precipitate of Tin p-Hydroxyphenylarsonate

First variant. The washed precipitate of tin p-hydroxyphenylarsonate is dissolved in 10% ammonia. The solution is placed in a standard flask and made up to the respective volume. 20-25 ml of the solution is transferred to a 200-250 ml flask with a ground glass neck, and hydrochloric acid is added in such amount that the acid concentration will be 1-2 N; 0.5 g of potassium bromide and excess of 0.1N $KBrO_3$ are then added and the solution allowed to stand for 15 minutes with frequent shaking. The hydroxyphenylarsonic acid is thereby converted into a tribomophenol.

When bromination is complete 0.1N As_2O_3 is added, and excess titrated against the same solution of $KBrO_3$ used previously, using indigocarmine as indicator. 1 ml of 1N $KBrO_3$ = 0.459 g tin p-hydroxyphenylarsonate or 0.009894 g Sn.

Second variant. This variant differs from the first only in that the tin p-hydroxyphenylarsonate after precipitation and washing is dissolved in concentrated hydrochloric acid by warming on a water bath. In this method, therefore, the filter plus precipitate are transferred to a flask fitted with a ground glass stopper, concentrated hydrochloric acid[1] added, and the solution heated on a water bath until complete solution of the precipitate is effected. Subsequent operations are the same as for the first variant. Results of tin determinations by the two variants are given in Table 1.

TABLE 1

Amount of tin in 1 ml solution, in g	1st Variant			2nd Variant	
	Amount of tin p-hydroxyphenylarsonate			Amount of tin p-hydroxyphenylarsonate	
	Taken, in g	Found, in g	Difference, taken − found, in g	Found, in g	Difference, taken − found, in g
0.001395	0.06474	0.06452	− 0.00022	0.06496	+ 0.00022
0.001395	0.06474	0.06463	− 0.00011	0.06474	0.00000
0.001395	0.06474	0.06474	0.00000	0.06485	+ 0.00011
0.001395	0.06474	0.06452	− 0.00022	0.06474	0.00000
0.001395	0.06474	0.06474	0.00000	0.06485	+ 0.00011
0.001395	0.06474	0.06452	− 0.00022	0.06463	− 0.00011
0.001395	0.06474	0.06474	0.00000	0.06474	0.00000

Note. In all the experiments (Tables 1, 2, and 3), the amount of tin solution to be titrated was 10 ml.

The results given in Table 1 show that both variants give good results even for fairly small amounts of tin in the test solution.

[1] 5N acid may be used if heating is carried on for half an hour.

Table 2 contains results of the determination of tin by the same method but with the difference that the acid concentration in the solution to be titrated was made up to 0.5% while the tin concentration was lowered to 0.00109 g.

TABLE 2

Amount of tin in 1 ml solution, in g	Amount of tin p-hydroxyphenylarsonate		
	Taken, in g	Found, in g	Difference, taken − found, in g
0.00109	0.0506	0.0505	− 0.0001
0.00109	0.0506	0.0504	− 0.0002
0.00109	0.0506	0.0505	− 0.0001
0.00109	0.0506	0.0506	− 0.0000
0.00109	0.0506	0.0504	− 0.0002
0.00109	0.0506	0.0505	− 0.0001

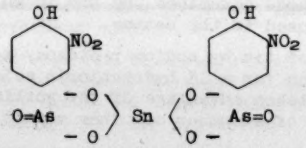
The results in Table 2 show that for 0.5% acid in the test solution, the results are even more accurate. This fact should make it possible to determine tin in the presence of other elements whose arsonates are soluble at that acid concentration.

One of the drawbacks of the method described is the necessity of heating the precipitate for a long time with concentrated hydrochloric acid to dissolve it. The use of ammonia as a solvent (first variant) has the disadvantage that bromination occurs in a heterogeneous medium, which is not convenient. In trying to get a more rational method for the determination of tin, we used p-hydroxy-m-nitrophenylarsonic acid (the uni-sodium salt of p-hydroxy-m-nitrophenylarsonic acid) instead of sodium p-hydroxyphenylarsonate in the following experiments.

Determination of Tin by Means of Sodium p-hydroxy-m-nitrophenylarsonate

The solution of tin to be analyzed is prepared as for determination by means of sodium p-hydroxyphenylarsonate. A threefold excess of precipitant is used (a 5% aqueous solution of sodium p-hydroxy-m-nitrophenylarsonate). As soon as the precipitant is added, a precipitate of tin p-hydroxy-m-nitrophenylarsonate, which is of a light cream color, forms.[1])

Analysis of the precipitate indicates the following formula for tin p-hydroxy-m-nitrophenylarsonate:



The precipitate is allowed to stand in the solution for 1 hour. At the end of this time, it is filtered and then washed on the filter 5-6 times with water or 2-3 times with 1N hydrochloric acid. After washing, precipitate and filter are placed in a wide necked flask and 25 ml of 2N hydrochloric acid added, the mixture is heated on a water bath until the precipitate has dissolved completely (30 minutes). This solution is transferred to a 100 ml standard flask and diluted to the mark with 2N hydrochloric acid.

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1) When there is even only 4μ g of Sn in 1 ml of solution, the formation of a precipitate by addition of p-hydroxy-m-nitrophenylarsonic acid and p-hydroxyphenylarsonic acid is still fairly easily observable.

20-25 ml of solution is taken for each determination. Conditions for bromometric determination are the same as for determination by means of sodium p-hydroxyphenylarsonate. The only difference is that on bromination of p-hydroxy-m-nitrophenylarsonic acid the dibromo derivative is obtained. (The equivalent weight of tin p-hydroxy-m-nitrophenylarsonate is M/8). Results of tin determinations by this method are given in Table 3.

TABLE 3

Amount of tin in 1 ml of solution, in g	Tin found, in g	Difference, taken − found, in g	Observations
0.00198	0.0199	+ 0.0001	Starting with the fifth experiment, the acid concentration in the test solution was made up to 1%.
0.00198	0.0198	0.0000	
0.00198	0.0196	− 0.0002	
0.00198	0.0196	− 0.0002	
0.00218	0.0216	− 0.0002	
0.00218	0.0218	0.0000	
0.00218	0.0216	− 0.0002	
0.00218	0.0217	− 0.0001	

The results of this last series of tests indicate that determination of tin by means of sodium p-hydroxy-m-nitrophenylarsonate is fairly accurate even for a concentration of 1% acid in the test solution and has the following advantages over the method involving sodium p-hydroxyphenylarsonate as precipitant:

1) tin p-hydroxy-m-nitrophenylarsonate does not require heating for precipitation;

2) tin p-hydroxy-m-nitrophenylarsonate dissolves comparatively easily on heating in 2N HCl, so that there is no need to heat it in concentrated hydrochloric acid (which is one of the drawbacks of the method involving sodium p-hydroxyphenylarsonate);

3) the precipitate of tin p-hydroxy-m-nitrophenylarsonate is easier to handle during all the operations than that of tin p-hydroxyphenylarsonate.

SUMMARY

1. New methods have been worked out for the volumetric determination of tin by means of sodium p-hydroxyphenylarsonate and sodium p-hydroxy-m-nitrophenylarsonate.

2. Of the two methods described the one in which sodium p-hydroxy-m-nitrophenylarsonate is used is the better.

3. Precipitation of tin by sodium p-hydroxy-m-nitrophenylarsonate proceeds quantitatively even for a 1% hydrochloric acid concentration in the test solution. This may be taken advantage of for working out a method of determining tin in the presence of a number of other metals which often accompany tin.

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CHRONICLE

Nikolai Aleksandrovich Tananaev

(On his 75th birthday)

This year the Chemical Society of our country celebrates the 75th birthday and the 45th year of scientific and teaching activity of one of the oldest analytical chemists, a Stalin Laureate, and a doctor of chemical sciences, Professor Nikolai Aleksandrovich Tananaev.

The development of Soviet analytical chemistry during the last 30 years has been closely connected with the name of Tananaev, who is one of the outstanding scientists in this branch of chemistry.

Spot analysis, which was first developed by Tananaev in the Soviet Union, has now been widely developed. This method is of great practical importance. Special reactions proposed by Tananaev and the systematic system of analysis based on these reactions, as well as the new method of "in situ analysis" are of great value in analytical chemistry.

N. A. Tananaev has always followed new paths in his scientific and teaching activities, as a result of which he has worked out new methods of chemical analysis and written original text books in analytical chemistry, such as 'Spot Tests,' 'Special Reactions and a Systematic Analysis Based on Them,' and 'In Situ Analysis.'

Tananaev has paid a lot of attention to volumetric and gravimetric analysis, and in these fields he has carried out many investigations. On his own, and in conjunction with his students, he has published ca. 200 papers.

Of particular value in Tananaev's scientific research activity is the intimate relation between theory and practice.

N. A. Tananaev is a wonderful teacher who has educated many cadres of analytical chemists and many of his pupils have turned out to be leading specialists in this branch of chemistry. His books "Volumetric Analysis," "Gravimetric Analysis," and "Analytical Chemistry," have been text books for a whole generation of analytical chemists. These books have played an important part in making analytical chemistry an independent subject.

His activities have been rewarded with awards and prizes by the Soviet Government. He has received the following awards: Order of Lenin, Order of Merit, A Medal for Work in the Great War, and A Medal for Ferrous Metallurgy. N. A. Tananaev received a Stalin Prize for his work on "In Situ Methods."

The Editorial Board of the Journal of Analytical Chemistry and a wide circle of Soviet analytical chemists, friends, and scientists wish Nikolai Aleksandrovich the best of health, and further successes in his work for the good of our country.

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Izrail Mironovich Korenman

(On his 50th birthday)

During January 1954 Izrail Mironovich Korenman who is a professor, a doctor of chemical sciences, and head of the chair of Analytical Chemistry in Gorky State University, celebrated his 50th birthday and his 25th year of activity as a scientist and teacher.

After finishing his course in the Odessa Chemico-Pharmaceutical Institute and getting his degree, Korenman was made a lecturer. Since 1937 he has been the head of the Analytical Section in Gorky State University. In 1940 he was made professor.

To date Korenman has published 230 papers including 5 monographs. He carried out his first scientific research during his student days. While still a candidate for his degree, he prepared a monograph on microcrystalloscopy which was issued in 1931 and was the first Soviet text book on this branch of analytical chemistry. He has successfully worked on the development of micro- and ultra-microchemical analysis; he has written a valuable text book· "Quantitative Microchemical Analysis."

Korenman has devoted considerable energy to working out and improving methods in sanitation and hygiene analysis. Some of the methods which have been worked out with his participation and the instructions drawn up on the basis of these methods have in no little degree contributed to improving the conditions of work in industrial enterprises. He started to work in organizations dealing with this type of work as long ago as 1928, and still continues to work with them.

In recent years Korenman has published many papers on the theory and practice of organic analytical reagents, in particular, on the development of views on so-called characteristic atomic groupings; the idea of "cyclic groupings" is his, these being the skeletal structures of characteristic groupings. He has described quite a few new color and microcrystalloscopic reactions with organic reagents for various elements. Korenman has described original flotation reactions for a large number of elements, whereby the selectivity and sensitivity of the basic reactions on which they are based can be increased considerably.

He has also been attracted to physico-chemical methods of analysis, and various physico-chemical researches: determination of the instability constants of complex ions, questions of the color of precipitates, questions of solubility, etc. He has also been occupied recently with the question of co-precipitation which is of very great importance in contemporary analytical chemistry.

Not only is he a foremost scientist, but he takes an active part in social life. He initiated and organized the conference on analytical chemistry held at Gorky State University in 1952.

As an active member of the Russian Communist Party (from 1941), he has carried out social work in Gorky University, and heads the philosophy seminary in the House of Science. In 1951 he was awarded the Order of the Red Banner of Labor.

We wish Korenman who is celebrating his birthday the best of health and many, many years of fruitful work for the glory of our great country.

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A HORIZONTAL A.C. ARC AS SPECTRUM EXCITATION SOURCE FOR ORES AND MINERALS

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All-Union Scientific Research Institute
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Spectral analysis is widely used for the analysis of ores and minerals which are non-homogeneous and are non-conducting. The universal spectrum excitation source in these cases is the carbon arc, which can be relied on to ensure evaporation of all materials known to us and to get the spectrum of most of the elements.

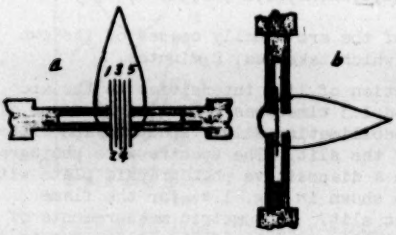

Fig. 1. Position of the arc flame reflection on the spectrograph slit when photographing spectra.

Quantitative analysis of ores and minerals, however, often present a difficult problem. The main reason for this is the fractional evaporation of elements, which is accompanied during evaporation of the test sample by concentration changes of the elements in the gas cloud round the arc and by changes in temperature of the arc flame [1]. This results in changes in the line intensity during the burning of the arc which are related to the composition of test material. One must also remember that the position of the arc flame itself is not usually characterized by its constancy with respect to the electrodes, and this in turn leads to an irregular behavior of the constancy of line intensity because of uneven element concentration distribution and irregular gas cloud temperature.

In the analysis of ores and minerals, therefore, it is of great importance to find conditions for test sample evaporation and arc burning conditions which will decrease the effect of fractional evaporation and also ensure a stable position for the arc flame; if this can be effected, conditions can also be so arranged that a flame is obtained, different parts of which differ considerably from each other in temperature and also in the concentration of the elements contained in it.

This will enable one to use those parts of the flame for which illumination of the lines of the test elements is optimal. These conditions are satisfied to some extent by simultaneous evaporation of the sample from two horizontally disposed A.C. carbon arc electrodes. When this arrangement of the elec-

trodes is adopted, a stable tongue of flame which is directed upward is formed, occupying the position shown in Fig. 1, a with respect to the electrodes.

According to our observations, the stability of the flame can be increased considerably by addition of compounds of elements with low ionization potentials to the test powders, since they favor the stabilization of the temperature of the arc flame during their evaporation.

Satisfactory results were obtained, e.g., by diluting the ore in a ratio of 1:2 to 1:5 with a mixture of 5 parts strontium sulfate and 8 parts of spectrographically pure graphite powder, and using sharpened carbon electrodes 8 mm long and 3 mm in diameter with openings 2 mm in diameter drilled in them. Sharpening of the electrodes and drilling of the holes were carried out with a special cutter and took 10-20 seconds.

When the arc was supplied with A.C. (15 A, 220 V, arc gap 4 mm), there was fairly regular intake of strontium into the arc flame, which coincides with the intake of the majority of the elements found in the middle of the volatility series for the elements given below [2].

The Intake Sequence of the Elements in the Arc Flame during Evaporation of Oxides from the Carbon Electrode Channel

Li, Na, K, Rb, Cs

(Hg, As, Cd, Zn, Bi, Sb, B, Pb, Tl, Mo, Sn, W), (Mn, Mg, Cu, Ge, In, Ga)

Rare earths

(Fe, Co, Ni, Ba, Sr, Ca, Si, Be, Al, V, Cr, Ti, U, Se, Mo, Re, Zr, Hf, Th, Nb, Ta, W, B)

One should note that the burning of the arc usually ceases of its own accord after evaporation of the sample, which takes ca. 2 minutes.

In order to determine the distribution of line intensities in the arc flame the image of the latter, decreased 1.3 times, was projected by means of a quartz lens on to the slit of an autocollimating Hilger spectrograph fitted with an antivignetting lens in front of the slit. The spectra were photographed in the course of 1 minute 30 seconds on a diapositive photographic plate with contrast factor of 1.6 in the positions shown in Fig. 1, a for the flame image with respect to the spectrographic slit. Photometric measurements of the spectral lines obtained for these positions of the flame allow one to deduce the distribution of the line intensity in various parts of the flame on going from bottom to top of the flame.[1)]

In order to get information about changes in line intensity in the part of the flame along the electrode axis, the spectra were photographed by turning the image of the flame through 90° (Fig. 1, b).

Rotation of the flame image is effected by means of the quartz prism set up in front of the slit, using total internal reflection obtained by the parallel position of the prism base in relation to the pencil of light.

The spectra were photographed in all cases through a net of parallel filaments fixed in front of the spectrograph slit; this ensured the appearance of longitudinal bright lines at equal distances from each other on the spectrogram. This enables one to determine easily to which part of the arc flame the various parts of the spectral line photographed correspond. The trans-

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1) I. V. Ilyasova took part in the work of getting spectrograms and establishing the distribution of line intensities in the arc cloud.

formation from the blackening values found for the different parts of the lines to their intensity was carried out by the usual method of using the characteristic curves of the photographic plate, the background of the spectra being taken into account.

By finding the distribution of the line intensity in the part of the flame between the electrodes, it is possible to control changes in the absolute value of the line intensities when getting spectra in other positions of the flame, and to express their line intensities in all cases on one scale. Lines for which the phenomenon of self-absorption were not observed were measured.

A study of the distribution of line intensities in the arc flame showed that when an A.C. arc is used, there is always obsefved a clearly expressed increase for both arc and spark lines near the electrodes, which is common to all the elements. This increase occurs independently of the ionization potential and atomic weight of the elements and of the volatility of the material of which the test element is a component.

As examples, we have adduced in Fig. 2 the characteristic changes in line intensity in the flame on going from one electrode to the other along the axis for the lines V I 3185.4, V II 3110.7, Be II 3131.1, Be I 2650.8 and Ba I 3071.6. These curves are the evaporation curves of quartz containing 0.03% of vanadium

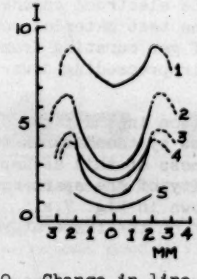

Fig. 2. Change in line intensity along the electrode axis. A.C. arc 220 V, 15 A. 1 – Be II 3131.1; 2 – V I 3185.4; 3 – V II 3110.7; 4 – Ba I 3071.6; 5 – Be I 2650.8.

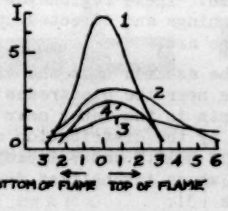

Fig. 3. Change in line intensity along the length of the flame. A.C. arc 220 V, 15 A. 1 – Be II 3131.1; 2 – V I 3185.4; 3 – Ba I 3071.6; 4 – V II 3110.7.

pentoxide, 0.02% beryllium oxide, and 0.5% barium oxide. Before the powders were placed in the electrode canals, they were diluted in the ratio 1:5 with a mixture of strontium sulfate and graphite.

The elements for which curves are adduced differ considerably both in ionization potentials (barium 5.2, vanadium 6.7, beryllium 9.3 eV) and in atomic weight (barium 137.4, vanadium 50.9, beryllium 9.0).

The transition from bottom to top of the flame is always accompanied by first, a regular increase, followed by a weakening in line intensity of the elements. The characteristic change in intensity for the vanadium, barium, and beryllium lines indicated above on passing through the center of the flame from bottom to top of the flame is shown in Fig. 3.

Fig. 4 depicts as an example, the change in the vanadium arc line of 3185.4 along the axis for the positions 1, 2, 3, 4, and 5 of Fig. 1, a, of the flame image on the spectrograph slit.

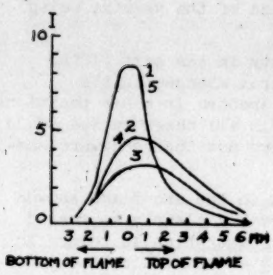

Fig. 4. Change in intensity of the V I 3185.4 line along the length of the flame for the positions of the flame indicated on Fig. 1,a.

A study of Fig. 4 shows that the greatest maxima are exhibited by the curves depicting the parts of the flame nearest the electrodes.

The regular character of the distribution of line intensities in an A.C. arc is shown up particularly clearly when curves are constructed which connect parts of the flame with equal line intensities; e.g., a study of Figs. 5 and 6 shows that the curves connecting the parts of equal intensity for the lines V I 3185.4 and V II 3110.7 and also Ba I 3071.6 and Be II 3131.1 are disposed symmetrically in the arc flame separating the regions of the flame with near values of line intensities. The transition on the drawings from one region of the flame to another is accompanied by a two-fold change in line intensity.

The regions of the arc flame radiating the lines of greatest intensity are always concentrated near the electrodes and touch the electrode channels, from which the gaseous products of the evaporation of the test material enter into the flame. These regions are reminiscent of jets of gas bursting from the electrode openings and directed upward by streams of air proceeding downward into the arc.

It can be assumed that the line intensity distribution in the parts of the arc flame near the electrodes is basically determined by the distribution of the elements in the vapor near the arc. The correctness of this assumption is borne out by the distribution of the relative intensity of the spark and arc lines V II 3110.7 and V I 3185.4 in the flame as shown in Fig. 7,a, the ratio of whose intensities depends to a large extent on the temperature of the arc flame [3].

In the central part of the flame the relative intensity of the lines indicated proved to be 0.7, while on passing into adjacent regions of the flame, this ratio was 0.6, 0.5, etc.

A comparison of Figs. 5, 6, and 7 shows that the distribution of line intensities of the elements in the flame does not agree with the distribution of the relative intensity of the vanadium lines, which indicates that in the central regions of the flame enclosed by the electrodes, no significant temperature changes were observed.

At the same time the distribution of the relative intensity of the spark and arc lines of vanadium shows that a transition from the center of the flame to its upper part should be accompanied by a regular temperature decrease, which undoubtedly should reflect on the intensity of the spectral lines. These conclusions were later confirmed by measuring the temperature and concentration of elements in various parts of the gas cloud round the arc.

The arc temperature was calculated from the ratio of intensities of the arc lines Bi 2938.32 and 2989.05 with known values of excitation energy and from the value of $A_{1k} \frac{g_1}{g_0}$ [4].

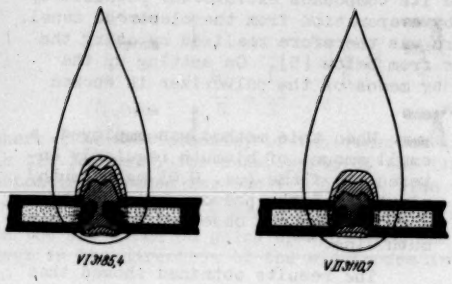

Fig. 5. Distribution of intensities of the lines V I 3185.4 and V II 3110.7 in the arc flame on evaporation of the test material from two electrodes. A.C. 20V, 15A.

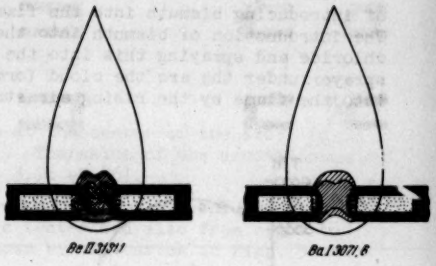

Fig. 6. Distribution of the intensities of the lines Be II 3131.1 and Ba I 3071.6 in the arc flame when the test material is evaporated from two electrodes. A.C. 220 V, 15 A.

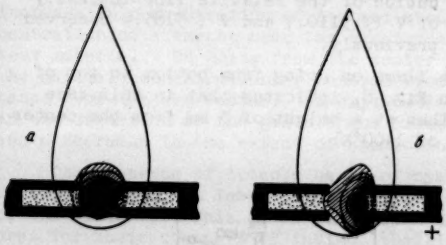

Fig. 7. Distribution of the relative intensity of the lines $\frac{\text{V II } 3110,7}{\text{V I } 3185,4}$ in the flame on evaporation of the test material from two electrodes. a) A.C. 220 V, 15 A; b) D.C. 180 V, 12 A.

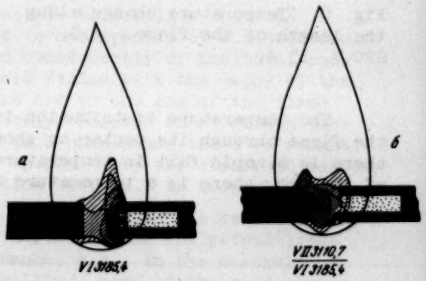

Fig. 11. Distribution of the intensity of the VI 3185.4 line and of the relative intensity of the lines $\frac{\text{V II } 3110,7}{\text{V I } 3185,4}$ in the arc flame on evaporation of test material from one electrode. A.C. 220 V, 15 A.

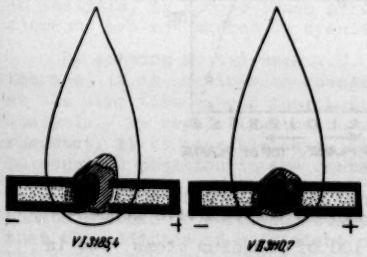

Fig. 13. Distribution of the line intensities of V I 3185.4 and V II 3110.7 in the arc flame on evaporation of test material from two electrodes. D.C. 180 V, 12 A.

Fig. 14. Distribution of intensity of the line Ba I 3071.8 in the arc flame during evaporation of test material from two electrodes. D.C. 180 V, 12 A.

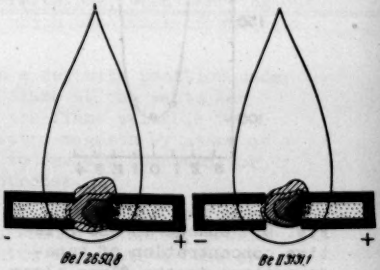

Fig. 15. Distribution of the intensities of the Be I 2650.8 and Be II 3131.1 lines in the arc flame during evaporation of test material from two electrodes. D.C. 180 V, 12 A.

The temperature was calculated by Ornshtein's method.

The high volatility of bismuth and its compounds excludesthe possibility of introducing bismuth into the flame by evaporation from the electrode canal. The introduction of bismuth into the arc was therefore realized by using the chloride and spraying this into the arc from below [5]. On setting up the sprayer under the arc the cloud formed by means of the pulverizer is sucked into the flame by the rising air stream.

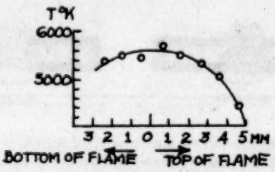

Fig. 8. Temperature change along the length of the flame. A.C. 220 V, 15 A.

When this method was employed, a small amount of bismuth regularly entered the flame (ca. 0.03 mg bismuth/minute) and the phenomenon of reabsorption was not observed for the bismuth line.

The results obtained showed that the temperature in the middle of the flame was 5300°K and changes to a comparatively small amount on going from the center of the flame to the electrodes. This agrees with the distribution of the relative line intensity of V II 3110.7 and V I 3185.4 observed previously.

The temperature distribution in the flame on going from bottom to top of the flame through its center as shown in Fig. 8, indicates that in this case there is a rapid fall in temperature. Thus at a height of 5 mm from the center of the arc, there is a temperature fall of 1400°K.

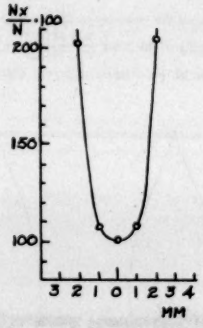

Fig. 9. Change in the relative concentration of vanadium atoms in the flame along the electrode axis. A.C. arc 220 V, 15 A.

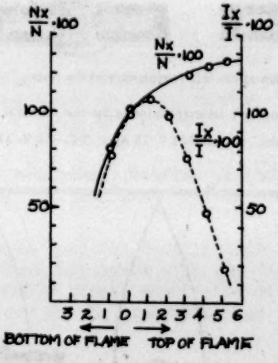

Fig. 10. Change in the relative concentration $\frac{N_x}{N} \cdot 100$ of vanadium atoms, and in the relative intensity $\frac{I_x}{I} \cdot 100$ of the V I 3185.4 line along the length of the flame. A.C. arc 220 V, 15 A.

By measuring the relative intensity of the arc lines 3185.4 of vanadium along their length and using the value of the arc temperature found, it is possible to calculate the distribution of the relative concentration of neutral

vanadium atoms in the arc flame. The following expression was used for calculating the relative concentration of vanadium atoms N_x/N:

$$\frac{N_x}{N} = \frac{I_x}{I} \cdot e^{-\frac{E}{K}\left(\frac{1}{T} - \frac{1}{T_x}\right)},$$

where I is the intensity of the vanadium line at the center of the arc; I_x is the intensity for other parts of the flame. The value of the excitation potential assumed for the V I 3185.4 line was 3.96 eV [6].

The distribution found for the relative concentration of vanadium atoms in the arc flame on going upward from the arc center and also from right to left in the direction of the electrodes is shown by the curves in Figs. 9 and 10.

At the same time the change in relative intensity of $\frac{I_x}{I}$ of the arc line of vanadium 3185.4 is shown in Fig. 10 for comparison.

On the basis of these diagrams, it is possible to conclude that the strengthening of the lines near the electrodes is accompanied by a considerable increase in concentration of neutral atoms, and consequently of the total concentration of elements near the electrode canals filled with the vapor of the test material. On going from the center of the arc to the end of the flame the maximal concentration of neutral atoms is only observed at a certain distance from the arc center. An explanation of this phenomenon is to be sought in the deviation of the gas streams errupting upward from the electrode canals, and a decrease in the extent of atomic ionization with fall in temperature.

The presence of intense bands of cyanide in the 3520-4220 A region of the carbon arc spectrum leads to overlapping of a series of the analytical lines of the elements. This is of particular importance, e.g., in the analysis of ores for their contents of indium, thallium, gallium, some of the rare earths, and also for strontium, barium, niobium, lead and other elements.

As our experiments showed, the fall in temperature on passing from the arc center to the end of the flame leads to a more rapid weakening of the cyanide bands in comparison with the analytical lines of a number of elements which usually possess low excitation potentials. This permits one, when carrying out an analysis, to choose those parts of the flame in which the lines of the test elements are not masked by cyanide bands.

By setting up two weak A.C. electro-magnets in a definite position under the arc, it is possible to change the shape of the flame as one wants, and at the same time extend the choice of the parts of the flame suitable for analysis. By regulating the current fed to the electro-magnets by means of a rheostat, it is possible, e.g., to force the flame to deviate downward or to occupy a position in the center between the electrodes.

Weakening of the cyanide band can be effected by addition of sodium carbonate instead of strontium sulfate to the ore. It should be noted, however, that the addition of sufficient of the volatile sodium carbonate to the ore led to a comparatively brief decrease in arc temperature. Consequently sodium carbonate can only be used for the analysis of elements which proceed from ore to arc flame at the same time as the sodium carbonate. These properties are exhibited by the elements which are found at the beginning, and in a bit of the middle of the volatility series adduced above for element oxides in the carbon arc.

Prolonged weakening of the cyanide bands and simultaneous stabilization of flame temperature can be achieved by the simple introduction of a cotton

wick with sodium carbonate, or a glass rod [8], into the arc flame from below.

Stabilization of arc temperature by the introduction of compounds of elements with low excitation potentials into one of the electrodes and evaporation of the test sample from the other electrode is of undoubted interest for the spectral analysis of ores and minerals. Unfortunately, in this case observation did not lead to positive results since the unsymmetrical evaporation of test material from the horizontally disposed electrodes caused an extremely uneven distribution of line intensities in the arc cloud. As an example, we have adduced in Fig. 11, a the distribution of intensities of the V I 3185.4 line on evaporation of the test material from the canal of one of the electrodes. It should be noted that evaporation of test material from one electrode also leads to a very significant change in excitation conditions on going from one part of the flame to another. Fig. 11, b corroborates this; here is shown the change in relative intensity of the lines V II 3110.7 and V I 3185.4.

As already indicated simultaneous evaporation of test sample in an A.C. arc from two horizontally disposed electrodes always leads to a symmetrical distribution of line intensities in the arc cloud which is practically independent of the composition of test sample and the properties of the elements. Replacement of A.C. by D.C. leads to a distribution of line intensities which is uneven and which also depends on test composition and properties of the elements. When D. C. is used the polarity of the electrodes is clearly manifest; this polarity destroys the concentration distribution of the elements in the arc cloud and leads to a strengthening near the cathode of elements with comparatively low ionization potentials [7]. The latter is known to take place as a result of the attraction of positively charged ions by the cathode, and consequently there is an increase in element concentration near the cathode.

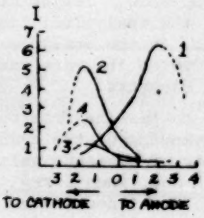

Fig. 12. Change in line intensity in the flame along the electrode axis. D.C. Arc 180 V, 12 A. 1 – Be II 3131.1; 2 – V I 3185.4; 3 – V II 3110.7; 4 – Ba I 3071.6

This strengthening of lines near the cathode was clearly observed, e.g., for the arc and spark lines of vanadium, and particularly for barium, which has a low value for the ionization potential (Fig. 12).

On the other hand, in the case of beryllium, which has a fairly high ionization potential, there was observed a strengthening of the lines near the anode. This can be explained on the grounds that the temperature of the anode is higher than the cathode, thus leading to a more rapid evaporation of material from the anode canal.

The overall picture of intensity distribution for the lines V I 3185.4, V II 3110.7, Be II 3131.1 and Ba I 3071.6 for a D.C. arc is illustrated in Figs. 13, 14, and 15.

The distribution of relative intensity of the V II 3110.7 and V I 3185.4 lines in the arc flame indicates non-uniformity of the excitation conditions in different parts of the D. C. arc (Fig. 7, b).

SUMMARY

1. A horizontal carbon arc between electrodes filled with test material is a valuable excitation source for ores and minerals.

2. The general uniformity of the symmetrical distribution of the intensi-

ties of arc and spark lines of elements in a horizontal A.C. arc has been demonstrated; this distribution is practically independent of the properties of the elements and of the volatility of the compounds.

3. It has been shown that the distribution of line intensities in a D.C. arc, in contrast to that in an A.C. arc, is of a complex nature and depends on the properties of the elements.

4. An explanation of the distribution line intensities in the arc flame has been given which is based on measurements of temperature distribution and of the distribution of the relative concentration of the atoms in the arc.

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ULTRAVIOLET COLORIMETRIC DETERMINATION OF SMALL AMOUNTS OF KETONES

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The A. A. Zhdanov Leningrad State University

The methods which are most widely used at present for the quantitative determination of ketones have been worked out as a rule with an eye to the analysis of acetone. Their sensitivity varies within the limits 10^{-3} to 10^{-4} % acetone in the test material [1-6]. A nephelometric method of determining acetone proposed by Shikhvargen, according to the author, permits a quantitative determination of acetone to be made down to concentrations in solution of $5 \cdot 10^{-5}$ %.

In previous papers [7,8], we have observed that the application of the iodoform reaction, and subsequent colorimetric determination in the ultraviolet of the iodoform formed during the reaction to the determination of acetone, methylethylketone, and methylpropylketone, enables the sensitivity of the quantitative determination of these ketones to be increased to $2 \cdot 10^{-5}$ %.

In the present paper, we give the results of a systematic investigation of the applicability of the method indicated to the quantitative analysis of aliphatic ketones. As test materials we used aqueous solutions of the following ketones: acetone, methylethylketone, pentanone-2, hexanone-2, heptanone-2, and octanone-2.

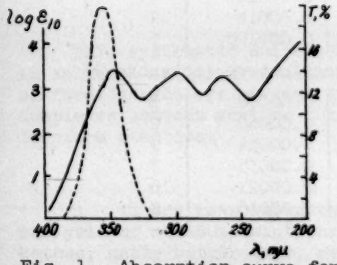

Fig. 1. Absorption curve for iodoform — full line; transmission curve for the light filter used — dotted line; T % — transmission of light filter in percentage; ϵ_{10} — molar absorption coefficient of iodoform.

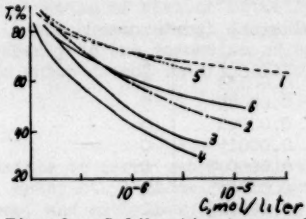

Fig. 2. Calibration curve for ketones.
1 — Acetone; 2 — Methylethylketone; 3 — Heptanone-2; 4 — Hexanone-2; 5 — Heptanone-2; 6 — Octanone-2; T % — Transmission of solutions in percentage; cuvette length — 2 cm.

All the ketones listed should give the iodoform reaction in accordance with the equation:

$$CH_3-CO-R + 3I_2 + 4NaOH = CHI_3 + R-COONa + 3NaI + 3H_2O.$$

In the course of this work we held to the following sequence of operations: 20 ml of iodine solution of the composition 200 g KI + 100 g I_2 + 400 ml H_2O was placed in a water-cooled separating funnel and 6.6 ml of 20% NaOH and 20 ml of test solution containing the test ketone added. The funnel was stoppered and shaken vigorously for 5 minutes, and excess iodine removed by addition of a few drops of 5% hyposulfite.

The iodoform which separated was extracted with 20 ml of pure chloroform (or with the same amount of ether dried over metallic sodium), the extract was transferred to a cylindrical cuvette provided with quartz windows, and the solution colorimetrically measured in the absorptiometer described by us previously [9].

TABLE 1

Weight of ketone taken, in %	Found, Δ in %	c/c %
Acetone		
0.00150	0.00150	0
0.00094	0.00093	1
0.00042	0.00041	2.5
0.00021	0.00020	5
0.000180	0.000186	3
0.000068	0.000070	3
0.000033	0.000035	8
Methylethylketone		
0.00173	0.00180	4
0.00067	0.00066	1.5
0.00040	0.00039	2.5
0.00025	0.00025	0
0.000173	0.000185	7
0.000069	0.000065	6
0.000032	0.000028	13
Methylpropylketone (pentanone-2)		
0.00177	0.00174	2
0.00130	0.00134	5
0.00042	0.00045	5
0.00022	0.00021	5
0.00015	0.00015	0
0.000075	0.000075	0
0.000040	0.000035	12
0.000018	0.000029	11

TABLE 2

Weight of ketone taken, in %	Found, Δ in %	c/c %
Methylbutylketone (hexanone-2)		
0.00205	0.00200	2.5
0.00102	0.00098	4
0.00078	0.00081	4
0.00025	0.00024	4
0.000110	0.000116	6
0.000076	0.000073	4
0.000042	0.000048	15
0.000021	0.000018	16
Methylamylketone (heptanone-2)		
0.00143	0.00137	4
0.00071	0.00067	6
0.00061	0.00058	5
0.00057	0.00060	6
0.00020	0.00020	0
0.00012	0.00014	17
0.000099	0.000105	5
Methylhexylketone (octanone-2)		
0.00090	0.00088	3
0.00063	0.00062	2
0.00055	0.00054	2
0.00038	0.00035	7
0.00025	0.00021	16
0.00016	0.00016	0

The iodoform absorption curve adduced in Fig. 1 shows that the greatest sensitivity of determination is achieved by carrying out colorimetric determination with a filter which isolates the spectrum at 360 mμ, since the absorption coefficient of iodoform in this region has a value of ca. 7000 cm^2/mol.

The transmission curve of the light filter used by us in the present work is adduced in Fig. 1 as the dotted curve.

Calibration curves for the ketones studied for a cuvette length of 2 cm are adduced in Fig. 2. Despite the fact that the time taken to carry out the iodoform reaction was varied from 5-20 minutes, we did not succeed in getting coincident curves, which suggests that there is a considerable difference in the rate of the iodoform reaction for ketones of different molecular weight.

Some of the results which were obtained during the analysis of ketone solutions are adduced in Tables 1 and 2. The rather large volume of the cuvettes we used did not permit us to cut down on the volume of liquid used for extraction of the iodoform. Despite this the sensitivity of determination was equal in some cases to twice that of Shikhvargen's nephelometric method. Increased length of cuvette and a smaller volume of extracting solvent should increase the sensitivity considerably, so that it should approximate to 10^{-6}% of ketone in the test mixture.

In parallel with the study of the sensitivity of colorimetric determination in the ultraviolet of aliphatic ketones, we also carried out some experiments on the analysis of mixtures of acetone with formaldehyde with the object of finding out the possibility of determining acetone colorimetrically in the presence of large amounts of the second component.

Some of the results obtained for mixtures of acetone and formaldehyde are given in Table 3. These results show that for a ratio of acetone to formaldehyde greater than 1:100, the concentration of acetone actually found was considerably lower than its real value. Up to this ratio, acetone was determined quantitatively with a relative error varying from 0 to 20%.

TABLE 3

Expt. No.	Amount of acetone taken in %	Amount of formaldehyde taken in %	Transmission of solution	Amount of acetone found in %	$\Delta c/c$ %
1	$3.97 \cdot 10^{-4}$	0	70	$3.97 \cdot 10^{-4}$	0
2	$3.97 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	70	$3.97 \cdot 10^{-4}$	0
3	$3.97 \cdot 10^{-4}$	$4 \cdot 10^{-3}$	72.5	$3.50 \cdot 10^{-4}$	12
4	$3.97 \cdot 10^{-4}$	$4 \cdot 10^{-2}$	74	$3.15 \cdot 10^{-4}$	21
5	$3.97 \cdot 10^{-4}$	$4 \cdot 10^{-1}$	83	$2.40 \cdot 10^{-4}$	40
6	$3.97 \cdot 10^{-4}$	4	93.5	$0.7 \cdot 10^{-5}$	82

This systematic decrease in the concentration of acetone actually found in solution as compared with its true value which occurs when large amounts of formaldehyde are present is related probably to the formation of stable complexes between acetone and formaldehyde which do not readily undergo the iodoform reaction.

SUMMARY

1. It has been shown that it is possible to carry out quantitative analysis of aqueous solutions of acetone, methylethylketone, methylpropylketone, methylbutylketone, methylamylketone, and methylhexylketone by colorimetric determination in the ultraviolet using the iodoform reaction. The sensitivity is $2 \cdot 10^{-5}$%, the relative error 0-15%, and the time taken to make a determination 15-20 minutes.

2. It has been established that colorimetric determination of acetone in solution in the presence of formaldehyde is possible for ratios of acetone

to formaldehyde up to 1:100.

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DETERMINATION OF BERYLLIUM IN BRONZE BY MEANS OF A CATION EXCHANGE RESIN (CATIONITE)

D. I. Ryabchikov and V. E. Bukhtiarov

In order to get accurate results during beryllium determination, it is essential to separate it from many elements which accompany it, including aluminum and iron. Since, however, beryllium resembles aluminum in its chemical properties, separation from the other presents certain difficulties.

The following methods are in current use for the separation of beryllium from aluminum and iron; the acetate-tannin ortho-hydroxyquinoline method [1], the carbonate method, and also a method based on the difference in the hydrolytic properties of beryllium and aluminum succinates, respectively [2].

Many of the methods enumerated above take a long time to carry out, require expensive reagents and do not ensure the necessary accuracy. We set ourselves the task of finding a method which is free from these objections.

On the basis of preliminary experiments it was established that the easiest way of solving the problem was to separate beryllium from aluminum and iron chromatographically.

The basis of this separation of beryllium from aluminum and iron was their capacity to form complex compounds with oxalic acid according to the following equations:

$$AlCl_3 + 3H_2C_2O_4 = H_3[Al(C_2O_4)_3] + 3HCl;$$

$$FeCl_3 + 3H_2C_2O_4 = H_3[Fe(C_2O_4)_3] + 3HCl;$$

$$BeCl_2 + 2H_2C_2O_4 = H_2[Be(C_2O_4)_2] + 2HCl.$$

Although all these metals form complex oxalates, their respective oxalates differ considerably from each other in stability. Thus, the complex oxalates of aluminum and iron maintain the coordinate sphere in weakly acid solution (pH 4.4-5), while complex beryllium oxalate is stable in neutral or weakly alkaline solutions.

It is just this difference in the stability of the respective complex oxalates of bivalent beryllium and trivalent aluminum and iron which is a function of the pH that was used for their separation. The cation exchange resin used was SBS as before [3], 15 g of which was placed in a 100 ml buret and transformed into the hydrogen form before use. Initially an attempt was made to separate beryllium from aluminum and iron after their absorption by the cation exchange resin. This was carried out as follows: To the weakly acid solution containing beryllium, aluminum, and iron, ammonia was added until a turbidity appeared which was then removed by addition of a few drops of hydrochloric acid. The solution thus obtained was passed through a column at a rate of 2 ml/minute. Under these conditions, the ions of all these metals are absorbed by the cation exchange resin. The column was then eluted with 2% oxalic acid until all the aluminum and iron had been extracted; removal of all the iron was checked by testing with potassium thiocyanate. After removal of

aluminum and iron with oxalic acid, the beryllium was extracted from the cation exchange resin by passing through 10% hydrochloric acid. It was then precipitated in the filtrate with ammonia and determined gravimetrically. Results of determination of beryllium in solutions containing aluminum and iron are adduced in Table 1.

TABLE 1

Amount taken, in mg			Amount of Be found, in mg	
Be	Al	Fe		
9.2	1.3	2.2	8.6	9.1
			9.1	8.8
			8.9	9.0

Although satisfactory results were obtained for beryllium by this method, it cannot be applied for this purpose, because extraction of aluminum and iron from the cation exchange resin by oxalic acid is very slow. Another separation technique was therefore employed; aluminum and iron were complexed as oxalates before passing the original solution through the column. To the weakly acid solution containing beryllium, aluminum, and iron, was added a 2% solution of oxalic acid followed by ammonia dropwise until an alkaline reaction to methyl orange (pH 4.4) was obtained. This solution was then passed through a column at a rate of 2 ml/minute; when this was done, the aluminum and iron in the form of complex anions $[Me(C_2O_4)_3]^{3-}$ passed through into the filtrate while beryllium was absorbed on the cation exchange resin. After washing the column with distilled water, the beryllium was extracted from the cation exchange resin with 10% hydrochloric acid, and the beryllium finally determined gravimetrically as before. Results for the determination of beryllium in solution containing aluminum and iron by the second method are adduced in Table 2.

TABLE 2

Amount taken, in mg			Amount of Be found, in mg
Be	Al	Fe	
4.0	1.3	2.2	4.3; 3.9; 3.8
10.0	1.3	2.2	9.6; 10.0; 9.9
14.0	1.3	2.2	14.1; 13.8; 13.7

The results obtained for beryllium are completely satisfactory, as the table shows, and in this case, the time required for separation of beryllium from aluminum and iron under conditions where test material is given a preliminary treatment with a complexing agent is much shorter.

This method worked out for the determination of beryllium in the presence of aluminum and iron in synthetic mixtures by means of the cation exchange resin SBS was subsequently applied for the determination of beryllium in bronzes. In addition to the chief components (copper and beryllium) of the beryllium bronzes used, there was a number of other metals present, the chief of which were iron (up to 0.4%) and aluminum (up to 0.25%).

The following procedure was adopted for the analysis of bronzes: 0.5 g of the alloys was dissolved on heating in 25 ml of 30% nitric acid, and copper removed electrolytically in the solution obtained.

To this solution free of copper, ammonia was added until a faint odor was observed, when it was heated, and after 10 minutes filtered. The precipitate on the filter, which consisted of the hydroxides of beryllium, aluminum, and iron, was washed four times with a hot 2% solution of ammonium nitrate, and then dissolved in 20% hot hydrochloric acid. The filter was washed a few times with hot water. The solution was evaporated to a volume of 1 ml, after which it was cooled and diluted with 25 ml of water. To this solution was added 40 ml of 2% oxalic acid, 2 drops of methyl orange, and ammonia (dropwise) until the red color changed to yellow. This solution was passed through a column containing SBS in the hydrogen form at the rate of 2 ml/minute; beryllium was absorbed by the cation exchange resin while aluminum and iron passed into the filtrate. Traces of aluminum and iron were washed out of the column with water

at the rate of 4/5 ml/minute. Beryllium was completely removed from the column by eluting the column with 250 ml of hydrochloric acid. The filtrate containing the beryllium was treated with ammonia and then heated to 70°; after 10 minutes beryllium as hydroxide was filtered off through an ashless filter paper.

The precipitate was washed three times with hot 2% ammonium nitrate and after drying was calcined in a porcelain crucible at 1000° to give beryllium oxide.

The beryllium content was determined from the formula:

$$\% \text{ Be} = \frac{a \cdot 0.3605 \cdot 100}{m},$$

where a is the weight of beryllium oxide in g, 0.3605 is the conversion factor for beryllium oxide to beryllium, and m is the weight of sample taken, in g.

Results of beryllium determinations in bronzes by means of SBS are given in Table 3.

TABLE 3

Sample No.	Be found, in %		Be found, in % (gravimetrically with ammonia) after chromatographic separation.
	CO	Gravimetric (orthohydroxyquinoline method)	
110	2.12	2.23; 2.18; 2.22	2.07; 2.14; 2.08; 2.11; 2.10
452-1		2.18; 2.17; 2.20	2.08; 2.13; 2.08; 2.06; 2.07
452-2		2.19; 2.19; 2.23	2.14; 2.10; 2.12; 2.08.
455-1		2.26; 2.28; 2.26	2.28; 2.23; 2.20; 2.20; 2.26
455-2		2.23; 2.20; 2.17	2.10; 2.14; 2.14; 2.10; 2.10
3		2.17; 2.15	2.05; 2.01; 2.02; 2.04; 2.08

Comparison of the results obtained for beryllium by the chromatographic method with results obtained by other methods shows that the chromatographic method gives satisfactory results.

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ORGANIC COPRECIPITANTS (COLLECTORS)

I. THE THEORETICAL BASES OF ORGANIC COPRECIPITANT ACTION

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A number of scientific and technical circles are at present showing increased interest in the presence of extremely small concentrations of individual elements in various materials. This is very important, particularly for geochemistry [1].

In order to carry out some of the analytical operations necessary for dealing with these traces, the methods of ordinary analytical chemistry are often inadequate [2]. In this connection, therefore, a new technique has had to be developed which is sometimes called the analytical chemistry of traces. One of the characteristics of this technique is preliminary concentration of the element, which is carried out by suitable ordinary methods.

For this preliminary concentration of elements coprecipitation of the elements is used, in which specially chosen so-called coprecipitants or collectors are used.

The action of many of the inorganic coprecipitants used is closely related to adsorption phenomena, the basic ideas for the use of which for coprecipitation of steel are well known from the work of V. I. Khlopin, K. Fajans, and O Khan, et al. The theoretical and practical side of the question has been treated in O. Khan's monograph [10].

Apart from the occasional use of organic ion exchange materials for element concentration, coprecipitants are almost invariably inorganic compounds, the applicability of which is not uniform in all cases.

The ideal coprecipitants are, of course, the isotopes of the coprecipitated elements [10]. The application of this type of coprecipitant (carrier) is confined to cases of precipitation of radioactive isotopes and to special cases of mass spectroscopic determination. Compounds of elements with properties very similar to the elements to be precipitated are sometimes good coprecipitants. An instance of this type is precipitation of one rare earth by another of the same group; radium with barium [10], astatine with tellurium [13], and certain others.

Compounds of low solubility and with a strongly developed surface [2, 15], are often used as inorganic precipitants, e.g., ferric hydroxide, alumina, hydrated manganese dioxide, sulfides [8, 11, 15], etc. Methods of using this type of collector are described in modern books on the determination of traces of elements [9].

In rare instances, e.g., as in the case of mercury compounds [17], the inorganic coprecipitant may be readily volatile. Such coprecipitants can be easily removed simply by heating the precipitates. In general the separation of the coprecipitated element from the inorganic carrier necessitates, as a rule, carrying out special additional operations, which do not always lead to the desired results. This complicates the use of inorganic coprecipitants when attempts are made to separate the coprecipitated element in the pure state free from carrier.

Other important disadvantages of inorganic precipitants are that their selectivity is not high enough; this is connected with the tendency of inorganic coprecipitants to adsorb various ions strongly, and the practical impossibility of controlling their selectivity.

In some cases organic precipitants can be found whose precipitating qualities can be forecast on the basis of the general theory of the action of organic reagents. The behavior of organic precipitants is readily controlled, and their selective coprecipitation properties are superior to those of inorganic precipitants. Organic precipitants, as indicated below, have little tendency to adsorb other ions, and the precipitates obtained are consequently purer than when inorganic coprecipitants are used. Organic coprecipitants can be removed from the required precipitates by simple combustion, thereby leaving the coprecipitated element in a pure state. This facilitates subsequent determination of the concentrated elements by any method.

Organic precipitants have already been in use for some time [12, 16] for carrying out preliminary concentration of elements for subsequent determination by spectrographic, X-ray spectrographic, and other methods. Organic coprecipitants carry this a stage further by lowering even more the limit to which the elements can be concentrated before determination.

The Impossibility of a Direct Application of the Coprecipitation Mechanism of Inorganic Coprecipitants to Organic Coprecipitants

Organic "Analogs" of Inorganic Ions

Organic compounds are known which give certain precipitation reactions analogous to the precipitation reactions of a number of inorganic ions. Thus benzidine precipitates sulfate ions in the same way as barium and strontium, while chloroplatinate ions are precipitated by many amines as well as by potassium, rubidium, cesium and some other elements.

The precipitation reactions of the cation diphenyliodonium $(C_6H_5)_2I^+$ is so similar to the precipitation reactions of Tl^+ that diphenyliodonium has been called "synthetic thallium," in the literature [20]. The solubility of diphenyliodonium salts is similar to the solubility of thallium salts; a mixture of the salts of these cations is not easily separated into its constituents by simple recrystallization, though it can be done chromatographically.

Such identical behavior in certain cases, however, is accidental. Organic "analogs" of inorganic ions show only an accidental or partial identity of behavior with corresponding inorganic ions in relation to the low solubility of certain of their salts in water. This identical behavior does not extend to the solubility of their other salts, or to solubility of these salts in other solvents apart from water.

Complete identity between organic anions and inorganic salts is impossible since the organic "analogs" differ appreciably from the corresponding inorganic ions in size, charge density, structure, number of electrons and their distribution, and in general in most other respects. E.g., the radius of the barium atom is 1.35 Å, while that of its organic "analog" benzidine is $\sim \pm 5$ Å [3].

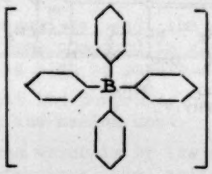
Salts of organic 'analogs' and salts of the respective inorganic ions do not form mixed crystals, are not isomorphous and are completely different crystallographically. This applies even to such closely related analogs as the diphenyliodonium cation and thallium [20]. As a result, difficultly soluble salts of organic analogs are not suitable coprecipitants for the respective inorganic ions. Attempts of the author to coprecipitate small amounts of strontium with the difficultly soluble benzidine sulfate did not give positive results.

Adsorption of Ions by Precipitates of Organic Compounds

Ionic adsorption on the surface of the precipitate formed is of great significance in coprecipitation with inorganic coprecipitants. The magnitude of this adsorption is closely related to the ionic character of the crystalline lattice of the precipitate and the presence of parts on the surface with strong fields.

Non-salt-like organic compounds crystallize in a molecular lattice. The crystal surface of these materials does not have areas with strong fields, so that the adsorption of ions on such crystals is manifest to only a very small degree. As a consequence of the large size of organic anions and cations, points with strong fields and a high charge density are absent even on crystals of salt-like organic compounds which, insofar as their capacity to adsorb ions is concerned, are inferior to inorganic materials.

There are direct indications in the literature of the incapacity of organic precipitates to adsorb ions. E.g., in a description of the removal of thionalide from solutions in the form of the disulfide, it is observed that in this case "the phenomenon of occlusion and adsorption is not manifest" [18]. An interesting example is the determination of potassium as $KB(C_6H_5)_4$. Here difficulties arise in connection with the volumetric variant of the determination. During volumetric determination of the boro-organic anion $B(C_6H_5)_4^-$ by titration with silver nitrate solution, which leads to the formation of a precipitate of $AgB(C_6H_5)_4$, the end point could not be determined when ordinary adsorption indicators were used, "...since the large $B(C_6H_5)_4^-$ anion adsorbs the silver salt only to an insignificant degree or not at all" [19].



These facts show up clearly the difficulty of trying to apply the known laws of inorganic adsorption to organic compounds, so that it would be unwise to search for organic coprecipitants, the action of which could be based only on adsorption phenomena. On the other hand, this weak tendency of organic precipitates to adsorb ions of elements is an advantage of organic coprecipitants, the action of which is based on other mechanisms, as this leads to the isolation of pure precipitates.

Coprecipitation with Organic Coprecipitants Considered as Extraction with "Solid Solvents"

The experiments described below show that effective organic coprecipitants can be easily sought if coprecipitation is considered as extraction with "solid extracting agents."

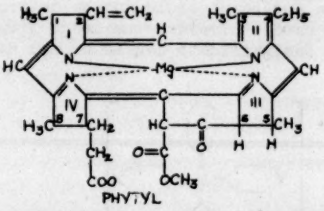
It is known that during precipitation of like materials, e.g., from an alcoholic solution by dilution with water, like materials precipitate simultaneously. The practice of purifying organic compounds shows that separation by similar methods, of mixtures of like materials, e.g., separation of members of a homologous series, is only carried out with great difficulty, the separation being more difficult the lower the solubility of the precipitated materials in dilute alcohol. By removal of one of the organic materials as a precipitate, it is possible to attract into the precipitate another similar organic compound of low solubility, traces of which were dissolved in the water or present in the water as a suspension.

In effect this process is completely analogous to extraction. It differs from ordinary extraction in that a solid material is used as the "extracting agent." If a suitable low melting product is used as a trapping agent, which on dilution of its alcoholic solution with water, separates out as a liquid, then the process will be a true extraction.

For successful coprecipitation, it is essential that there is the greatest possible similarity between the coprecipitated organic compound and the substance which is to be extracted as a precipitate. Numerous facts well known from the practice of purifying organic materials permit one to formulate the rule, "like precipitates like."

This rule which is completely analogous to the well known qualitative law defining the solubility of a substance, "like dissolves like," makes the search for organic coprecipitants of inorganic ions much easier.

Below we have adduced from P. Karrer's book [4], the formula of chlorophyll a, which contains magnesium.



One glance at this formula is enough to show that chlorophyll must be regarded as an organic material which has just these properties. Consequently, if when carrying out coprecipitation of magnesium it would be possible to convert magnesium into a compound similar to chlorophyll, coprecipitation of the compound obtained could be considered as coprecipitation of organic material.

As our experiments described below show, there is no need to convert the elements to be coprecipitated into such exceedingly complex compounds as chlorophyll in order to coprecipitate them. By successful choice of coprecipitant — excess of the precipitating organic reagent itself can sometimes be used — it is possible to effect coprecipitation by simply converting the element into a complex compound with such ordinary reagents as 8-hydroxyquinoline and similar precipitants.

In order to find out how far the action of organic coprecipitants of the category considered is comparable to extraction processes, two series of experiments were carried out in which the coprecipitant was the low melting product $C_6H_5 \cdot O \cdot C_6H_5$ (m.p. 27°). To a solution of cupric sulfate diluted to such an extent (5 μ g Cu in 250 ml) that 8-hydroxyquinoline does not give a direct precipitation of copper, was added with stirring an alcoholic solution of 2 mg of 8-hydroxyquinoline and 0.5 g diphenyl oxide. In one test the solution was heated up to 33° and the diphenyl oxide was in the form of an emulsion which, after cooling, set to a suspension. In the other test carried out at room temperature, a fine aqueous suspension of diphenyl oxide was first prepared, the copper solution was then added, followed by the 8-hydroxyquinoline. In both experiments the precipitates of diphenyl oxide were filtered, ashed, and copper determined in the residue. The amount of copper coprecipitated was the same in both cases, viz. 2.5 μ g.

These experiments and other similar ones show that in some cases at least, it is permissible to compare coprecipitation with extraction. This permits one to propose a priori that it is just as possible to extract elements from solution by coprecipitation as by extraction, from solutions just as dilute as can be handled by the latter. It should be remembered that extraction of the complexes of elements with organic precipitants can be more complete than direct precipitation with the same precipitants. This is well known from work on the complexes of 8-hydroxyquinoline [16], and others.

Coprecipitation with organic coprecipitants can also be compared with flotation reactions. This increases the number of compounds which can be dealt with, since in contrast to extraction in which all molecules must possess hydrophobic properties, for flotation reactions it is sufficient that only a part of the precipitated molecule should exhibit hydrophobic properties and have some properties in common with the precipitant.

Principles of Selecting Organic Precipitants

On the basis of the theoretical premises outlined above, which have also been checked experimentally, it is possible to select coprecipitants in practice by taking the following considerations for guidance.

1. When an organic reagent is used, the precipitated inorganic ion should be transformed into some compound in whose molecule the content of the organic part should be as high as possible.

2. It is desirable that the compounds of the element formed should be as insoluble as possible in the medium used.

3. Any organic compound which is of low solubility in the medium used and which has the closest structural similarity to the coprecipitated compound can be used as an organic coprecipitant of the compound of the inorganic ion obtained. It is convenient to introduce into the coprecipitant the same organic component which occurs in the coprecipitated compound of the test element.

4. In some cases the molecule of the organic coprecipitant may not have any great structural affinity with the molecule of the coprecipitated compound of the inorganic ion ("indifferent" coprecipitants, see below).

Coprecipitation of Normal Salts Containing an Organic Part with a High Molecular Weight

If the coprecipitated element is capable of forming complex anions, about which it is also possible to judge from the capacity of the element to give so-called colored solid phase reactions [7], then salts of organic cations which are practically insoluble, have a high ionic weight, and contain those

same addenda that were used for forming the complex anion of the element should be very suitable coprecipitants.

E.g., on the basis of colored solid phase reactions [5] and other facts, it is known that zinc forms a characteristic weakly dissociated anion $Zn(SCN)_4^{2-}$, in which form, using methyl violet and other basic dyes, zinc can be precipitated from fairly weak solutions. Zinc can, however, be coprecipitated from even more dilute solutions in conjunction with a precipitate of the relatively insoluble thiocyanate cation of methyl violet. On the basis of experiments carried out by the author together with E. S. Pashin and E. V. Mitrofanova, it was found convenient to carry out the test as follows: To a weakly acid solution containing traces of zinc was added a small amount of ammonium thiocyanate; this was followed by methyl violet, and after this some more ammonium thiocyanate sufficient for precipitation of the methyl violet cations as thiocyanate. The precipitate was filtered, washed, ashed, and the coprecipitated zinc determined in the residue. From a volume of 100 ml, 1 μg of zinc was coprecipitated completely.

In addition to zinc, other elements which form complex thiocyanate anions – Bi, Cu, and Cd and many others[1]) can be coprecipitated in exactly the same way as zinc with methyl violet thiocyanate.

It is convenient to coprecipitate elements forming complex iodide anions with the iodides of methyl violet, methyl blue, aminoazo compounds, and other basic dyes.

It is possible by similar means to coprecipitate the most varied complex anions and cations of elements. Cations can be coprecipitated as the salts of high molecular weight aliphatic or other acids, using these acids or their salts with organic bases as the coprecipitant.

If the basic dye used does not form a sufficiently insoluble salt with the anions used as addenda, then this basic dye can be precipitated by some other organic anion with a greater ionic weight. E.g., the ammonium salts of anthraquinone sulfonic acid and of the monosulfonic acids of azo-compounds, and many other compounds, are suitable.

Another example is the coprecipitation of phosphorus, which in the experiments of the author and E. S. Palshin was completely coprecipitated from 10^{-10}-10^{-11} M solutions of phosphates. Ammonium molybdate was added to the acidified solution of phosphate, and the mixture heated to form the phosphomolybdate heteropoly acid; methyl violet was then added, and in order to precipitate this, ammonium anthraquinone-α-sulfonate was added. The precipitate which separated out was filtered off, washed, and ashed.

Coprecipitation of Complex and Inner Complex Salts of the Elements. "Indifferent Coprecipitants."

The organic coprecipitants considered above may be regarded simply as excess of an organic precipitant of low solubility or of the practically insoluble salt of such a precipitant. The drawback of coprecipitants of this type is that their selectivity is not high enough. The highest selective coprecipitation is shown by indifferent coprecipitants by which we mean coprecipitants which do not contain components which cause direct precipitation of the elements. Indifferent coprecipitants fit very well into the class of

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1) A method described recently for purifying salts was based on this principle; salts of Ni, Mg, and Cr are purified from Zn, Cd, Hg, Bi, Co and Cu, the latter being completely precipitated after addition of thiocyanates and diantipyrylmethane hydrochloride [21].

"solid extracting agents." Coprecipitants of this type may be of a different kind altogether from the coprecipitated compound. Of particular interest are coprecipitants which do not contain salt-forming or complexing groups, since such coprecipitants show very little tendency to adsorption of ions from solution, and therefore give particularly pure precipitates.

The esters of the corresponding organic precipitates should from general considerations be particularly suitable as indifferent coprecipitants for the precipitation of inner complex salts of the elements. E.g., the dialkyl ester of dimethylglyoxime should be a suitable coprecipitant for the coprecipitation of nickel dimethylglyoxime. The esters of the precipitants are more suitable as coprecipitants than the organic precipitants themselves, since the inner complex compounds of the elements are more like the esters of the organic precipitants than the precipitant itself. The use of excess of an organic precipitant as a coprecipitant is less convenient, and a consequence of its use will be a less pure precipitate, as observed, e.g. in cupferron precipitates [14].

Apart from the coprecipitation of inner complex compounds, indifferent coprecipitants are equally suitable for the coprecipitation of compounds which are normal salts, e.g. for the precipitation of the salt of the methyl violet cation with the complex thiocyanate anion of zinc $Zn(SCN)_4^{2-}$.

The use of indifferent coprecipitants is particularly attractive because they do not require the introduction of large amounts of some other reagent to the solutions, e.g. addition of NH_4SCN as in coprecipitation with precipitates of methyl violet thiocyanate. Consequently when indifferent coprecipitants are used, current analytical methods in which selectivity has been thoroughly studied may be applied. E.g., zinc was precipitated successfully at a dilution of $1:10^7$ and in even more dilute solutions on using phenolphthalein as a coprecipitant and working directly under the conditions recommended for carrying out the highly selective colored solid-phase reaction for zinc with thiocyanates and methyl violet [5].

It is convenient to use indifferent coprecipitants in the form of their alcoholic or acetone solutions. On pouring these solutions into water, the dissolved coprecipitant separates out as a precipitate and traps the compound to be coprecipitated. There are as yet no general theoretical considerations which can be used as a basis of a search for the most suitable coprecipitant in each individual case. One must look for these coprecipitants experimentally, and this should not prove too difficult. E. V. Mitrofanova, while carrying out experiments on the precipitation of organic dyes of various classes from aqueous solutions, found that phenolphthalein, α-naphthol, m-nitrobenzoic acid, and β-hydroxynaphthoic acid are good coprecipitants.

Improving the Completeness of the Precipitation of Elements with Organic Precipitants.

The use of organic precipitants permits one to extend the limits of application of organic precipitation to solutions of lower concentrations of the elements to be precipitated. Such an extension of the limits can be realized by combining organic precipitants with extraction, as noted in the literature [10]. When organic precipitants are used, this is conveniently achieved.

In noting the great practical importance of the possibility of improving the completeness of precipitation of the elements by using organic precipitants, we shall confine ourselves to only one example. At a dilution of $1:10^7$, nickel is not precipitated by 8-hydroxyquinoline. Even when a large amount of macerated paper is used, no nickel is present in the paper mass filtered off. When however β-naphthol is used as a coprecipitant under the same conditions, complete precipitation of nickel is observed even at dilutions of $1:5\cdot10^8$ (E. V. Mitrofanova).

The Selective Action of Organic Coprecipitants

The selective action of coprecipitants which are salts of low solubility is fully understood.

All those elements which have ions identical in structure and properties with the coprecipitated ions of the elements being coprecipitated can be coprecipitated with this type of coprecipitant. E.g., on coprecipitating zinc in the form of the methyl violet salt with the anion $Zn(SCN)_4^{2-}$, all the other elements which form complex thiocyanate anions precipitated with methyl violet, i.e. Cd, Cu, and Hg, etc., will be trapped into the precipitate at the same time as the precipitate of methyl violet thiocyanate. In addition, all those other elements will be coprecipitated which are present in solution, generally in the form of large, hydrophobic anions which form salts of low solubility with such large cations as the methyl violet cation. Examples of such anions are the tungstates[1], heteropoly acids, and various complex anions such as $AuCl_4^-$, $SbCl_6^-$, et al. Coprecipitations of this type are completely understood and are easy to foresee.

The fact that the underlying mechanism of coprecipitation is clear in individual cases permits coprecipitation to be controlled. In order to prevent coprecipitation of individual elements, it is necessary to convert them into hydrophilic complexes by addition of tartrates, citrates, and similar hydrophilic masking complexing agents. If these complexing agents do not convert the element to be coprecipitated into hydrophilic ions as well, then the selectivity of coprecipitation can be increased. In general, the selective action of organic precipitants which are salts is low, the more so because the introduction of large amounts of the precipitating ions, e.g. thiocyanate ions during precipitation of methyl violet thiocyanate, favors conversion into precipitated complex ions even of elements which show little tendency to do so.

The selective action of indifferent coprecipitants is higher. Of particular value is the fact that these coprecipitants, as noted already, can be used directly in the reaction media which are recommended in current methods for the precipitation of elements and for colorimetric determinations on the basis of colored solid phase reactions. Coprecipitation selectivity is almost the same as the selectivity of the respective reactions. A displacement of equilibrium can only occur as a result of a particularly complete separation of an element from a system by coprecipitation.

Questions of increasing the selectivity of analytical reagents are the most difficult questions of contemporary analytical chemistry. At present the most real and positive method of solving this question of selectivity is to develop for each element "two different precipitants" which, apart from precipitation phenomena is of general interest for the analytical chemistry of a given element.

By this term "the two precipitant method" we mean the presence of two precipitants of a given element, in our case of two coprecipitants, which would precipitate a given element on the basis of reactions with two completely different mechanisms. E.g., one precipitant would precipitate the element as a cation, while the other precipitant would precipitate it in the form of some complex anion. During the first precipitation, other elements will be precipitated in addition to the element in which we are interested, but probably not all those originally present in solution; some of

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1) Coprecipitation of tungsten is incomplete in this case. Complete coprecipitation of tungsten at dilutions of $1:10^9$ and more is achieved by simultaneous addition of tannin (experiments of the author and E. S. Palshin).

the elements will have been removed. After filtration, the organic reagent contained in the precipitate will be destroyed by ignition, the residue dissolved, and a new precipitation carried out using the second precipitant, which is selected so that not one of the other elements which may be present in the first precipitate will be trapped in the precipitate of the second precipitation.

As an example of the application of this method in which two selected organic reagents are used, we shall quote the published method [6] of determining tin in complex mixtures. In this case, tin (Sn IV, β-compounds) is initially coprecipitated from an acid solution with anthraquinone-α-arsonic acid, Zr, Hf, Nb, Ta, and Ti being coprecipitated simultaneously. After destruction of the reagent left in the precipitate and dissolving the tin, the latter is colorimetrically determined with the reagent "antrazo" (anthraquinone-<1-azo-4>-dimethyl aniline) on the basis of a colored solid phase reaction in which the capacity of tin to form anions of the form $Me^{IV}Cl_6^{2-}$ x x ($SnCl_6^{2-}$) is used.

A technique similar to that of "the two-precipitant method" was used by V. T. Chuiko for coprecipitation of nickel in order to separate it from elements of the fourth analytical group [11].

Good results are also obtained when one precipitant is used and the two valency states of the element are made use of; in this case the element is precipitated when in one of these valency states and not in the other. According to the author's and G. Grinevich's work, trivalent (but not univalent) thallium is quantitatively precipitated even at dilutions of $1:10^{10}$ from 0.2 N HCl with the precipitate formed between p-dimethylaminobenzene and methyl orange. The procedure adopted, therefore, is first to keep the thallium in the univalent state and precipitate all those elements which can be precipitated by the precipitant used, then after oxidizing the Tl^{I} to Tl^{III} ($TlCl_4^-$) by addition of the same reagent, the thallium can be coprecipitated and separated from the other elements.

SUMMARY

Organic coprecipitants are of great interest for preliminary concentration of micro amounts of elements before determining them quantitatively by the usual methods. The advantage of organic coprecipitants as compared to inorganic coprecipitants are: ease of removal of organic coprecipitants from precipitates by simple ignition, the practical absence of adsorption of other ions by many organic precipitants, the ease with which coprecipitation can be controlled, their well-known selective action.

Coprecipitated elements must be converted into compounds of low solubility, which contain as much as possible of the organic component. The compound of the element obtained should, if possible, be similar to the practically insoluble organic compound acting as coprecipitant. Inner complex, complex, and also normal salts of the elements containing a large organic part are suitable for coprecipitation. E.g., the difficultly soluble salts of the cations of methyl violet or methylene blue with the complex anions of the elements are suitable. Practically insoluble salts of the same organic cations with heavy, volatile, inorganic or organic anions can be used as coprecipitants.

Non-salt-like organic compounds ("indifferent" coprecipitants) can also be used as coprecipitants; their action can be considered as "extraction with solid solvents." The use of "indifferent" coprecipitants permits the concentration limit at which elements can be removed by organic precipitants to be extended.

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[1)] See Consultants Bureau Translation, page 299.
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QUALITATIVE ANALYSIS OF SILICO-ORGANIC COMPOUNDS BY INFRARED ABSORPTION SPECTROSCOPY

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Chemical methods of analyzing silico-organic compounds which are based on the capacity of the test material to give some characteristic reaction, do not always permit the exact determination of the composition of the test product. On the other hand, physical and physico-chemical methods of analysis such as spectral molecular analysis in the infrared, permit the problem to be solved relatively easily to give reliable results.

Comparative test methods are usually used when dealing with the spectra of complex molecules. For this purpose the absorption spectra of a number of structurally similar compounds have been studied, e.g., of a homologous series, since this brings out the similarities and differences in the absorption spectra. Using this method it is possible to establish a number of principles and apply infrared spectroscopy to structural problems. E.g., the presence of $-CH_3$ and $=CH_2-$ in a molecule leads to absorption near 3 μ. A large amount of work which has been carried out along these lines has enabled us to establish that the respective absorption bands are determined by the vibrations of definite atomic groupings or bonds and are practically independent of the rest of the molecule [1,2]. Vibrations corresponding to characteristic frequencies are concentrated in one bond of the molecule (a definite atomic grouping), while the remaining atoms have no essential effect on them. That is why, e.g., the frequency of the C–H bond is maintained a constant in all the homologs, irrespective of the position of the molecule in a homologous series. By a study of these characteristic frequencies, it is possible to sort out the absorption spectra of complex molecules and to assign each characteristic band to its respective frequency and to clarify a number of structural characteristics of the molecules. The position of characteristic frequencies in a spectra can be displaced considerably under the influence of a number of factors, such as the mass of the neighboring atoms, the nature of the bond, etc. This shift can also occur when not only the atoms of a given bond vibrate but the rest of the molecule as well. E.g., the characteristic absorption band of the C–H bond can be shifted to either the short or long wave length side of the spectra according to the structure of the molecule.

By gathering all the experimental data available, tables have been compiled (Tables 1 and 2) [3], for the characteristic vibration frequencies of groups of atoms and of the most important bonds.

The infrared spectra of homologs and isomers as shown experimentally have much in common. Nevertheless, they are clearly distinguishable from each other since each individual substance has its own non-recurring spectrum. On the basis of the application of infrared absorption spectra, the following problems can be solved: the identification of a substance by means of its infrared spectrum, proving the presence of definite atomic groupings

and chemical bonds in a molecule, identification of mixture components, establishment of the presence of tautomeric forms, and determining small amounts of contaminants present in test mixtures, etc.

The infrared absorption spectra of silico-organic compounds have not hitherto been studied to any significant extent. Published data [4-7] is insufficient to establish with a reasonable degree of accuracy what absorption bands are determined by which specific atomic groupings, and to establish the characteristics of certain bonds.

In this paper the infrared absorption spectra of the most important silico-organic compounds have been studied.

TABLE 1

Characteristic Vibration Frequencies of Atomic Groups and of the Most Important Bonds in Organic Compounds

Group	Fundamental		Overtones									
	μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}
$=CH_2$ and $-CH_3$	3.39 3.48	2950 2870	1.74	5740	1.19	8400	0.909	11000	0.630	15860	0.549	18214
$=CD_2$ and $-CD_3$	4.54	2200	–	–	–	–	–	–	–	–	–	–
–OH (free)	2.75	3630	1.40	7100	0.961	10400	0.740	13500	–	–	–	–
–OH (bound)	2.98	3350	1.60	6250	1.04	9605	–	–	–	–	–	–
–OD (free)	3.29	3040	–	–	–	–	–	–	–	–	–	–
–OD (bound)	3.76	2660	–	–	–	–	–	–	–	–	–	–
=NH and $-NH_2$	3.03	3300	1.53	6530	1.04	9650	0.806	12400	0.666	15000	–	–
–SH	3.84	2600	2.00	5000	–	–	–	–	–	–	–	–
=C=C=	6.06	1650	–	–	–	–	–	–	–	–	–	–
$-C\equiv C-$	4.50	2220	–	–	–	–	–	–	–	–	–	–
$-NO_2$	7.24	1380	–	–	–	–	–	–	–	–	–	–
–N=C=S	4.55	2150	–	–	–	–	–	–	–	–	–	–
$-C\equiv N$	4.44	2250	–	–	–	–	–	–	–	–	–	–
=C=O	5.81	1720	2.90	3440	1.90	5260	1.45	6890	1.16	8600	0.970	10309

TABLE 2

Characteristic Vibration Frequencies of Atomic Groups and of the Most Important Bonds in Inorganic Compounds

Group	Fundamental		Overtones					
	μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}
$-NO_2$ (nitrite)	12.25	820	8.25	1220	7.65	1320	–	–
$-CO_3$ (carbonate)	14.25	700	11.50	870	9.50	1060	6.66	1500
$-NO_3$ (nitrate)	15.50	650	12.25	820	–	–	7.14	1400
$-ClO_3$ (chlorate)	23.00	434	16.00	624	10.50	950	10.06	994
$-BrO_3$ (bromate)	29.07	344	23.00	434	12.50	800	12.25	820
$-IO_3$ (iodate)	31.05	322	28.01	357	12.75	780	10.06	793

EXPERIMENTAL

The objects of our tests were certain compounds of the following types: alkoxy-, aroxysilanes, alkyl and arylalkoxysilanes, alkyl and arylsilanes, and siloxanes.

The basic materials were synthesized by published methods [8]. The synthesized compounds were carefully purified by chemical and physical methods.

Final separation of the chemically pure compounds was effected by means of a rectifying column.

Physical constants for the products obtained are given in Table 3.

TABLE 3

Physical Constants of the Silico-Organic Compounds Synthesized

Formula and Designation of Compound	B.p. and m.p. in °C	D_4^{20}	n_D^{20}
Tetramethoxysilane $(CH_3O)_4Si$	121.4	1.0390	1.3681
Tetraethoxysilane $(C_2H_5O)_4Si$	166	0.9345	1.3830
Tetrabutoxysilane $(n\text{-}C_4H_9O)_4Si$	151.5 (16 mm)	0.9528	1.4132
Tetraisoamyloxysilane $(i\text{-}C_5H_{11}O)_4Si$	175 (12 mm)	0.8760	1.4180
Tetraphenoxysilane $(C_6H_5O)_4Si$	418; 52	–	–
Tetramethylsilane $(CH_3)_4Si$	26.8 (756 mm)	0.6466	1.3590
Tetraphenylsilane $(C_6H_5)_4Si$	530; 233	1.078	–
Trimethylallylsilane $(CH_3)_3SiCH_2CH{=}CH_2$	85.4 (760 mm)	0.7195	1.4075
Dimethyldiethoxysilane $(CH_3)_2Si(OC_2H_5)_2$	114 (742 mm)	0.8395	1.3810
Trimethylethoxysilane $(CH_3)_3Si(OC_2H_5)$	75 (745 mm)	0.7573	1.3742
Hexamethyldisiloxane $(CH_3)_3SiOSi(CH_3)_3$	100 (742 mm)	0.7638	1.3773

The infrared absorption spectra of the silico-organic compounds were studied on a Hilger spectrometer. The infrared ray receiver was a thermocolumn with a silver-cadmium thermocouple; the source was a Silit resistor 96 mm long and 8 mm in diameter which was heated with a current of 16 A at 48 V.

In order to maintain the radiation from the Silit resistor constant, the current used was stabilized with a precision stabilizer.[1)]

1) The stabilizer was constructed specially for this work by V. D. Matveev, an assistant in the Institute.

Since silico-organic compounds absorb the infrared strongly, the absorption spectra were photographed in carbon tetrachloride solution. The carbon tetrachloride was specially purified.

Tetraphenylsilane was examined as a powder. Measurements were made in the 2-10 μ region. The transmission curves of the compounds studied are given in Figs. 1-12.

DISCUSSION OF RESULTS

As the transmission curves show, one of the characteristic features of the infrared absorption spectra of the silico-organic compounds is the presence of strong absorption bands at 7-10 μ (1429-1000 cm^{-1}). A band is observed at 7.9-8.0 μ (1266-1250 cm^{-1}) in the infrared spectra of all compounds in which there are methyl groups connected to silicon. According to published results an absorption band is observed at 7.25 μ (1379 cm^{-1}) in the absorption spectra of aliphatic hydrocarbons $R - CH_3$, which is determined by the deformation vibration of the $C\begin{matrix}H\\ -H\\ H\end{matrix}$ bonds in the CH_3 groups. The presence of a band at 7.9-8.0 μ (1266-1250 cm^{-1}) is therefore apparently the result of the vibration of the Si — C bond in the group $\equiv Si - CH_3$. This hypothesis is confirmed by the fact that in the spectra of silico-organic compounds where there is no $\equiv Si - CH_3$ group, e.g., in the spectra of alkoxy and aroxysilanes (esters of orthosilicic acid) with the general formula $Si(OR)_4$, the band with maximum absorption at 7.9-8.0 is absent.

A band is observed at 9.5-9.6 μ (1053-1042 cm^{-1}) in the infrared absorption spectrum of all the silico-organic compounds in which silicon is linked with oxygen.

A band with wave number 1111 cm^{-1} [9] is observed in carbon compounds which contain an ester link. This frequency is interpreted as a characteristic frequency of the C — O bond. It can be assumed therefore that the band at 9.5-9.6 μ (1053-1042 cm^{-1}) is determined by the longitudinal vibration of the Si — O bond.

Yet another band is observed at 8.6-8.7 μ (1163-1149 cm^{-1}) in the infrared spectrum of alkoxy-and aroxysilanes with the general formula $Si(OR)_4$, and in the spectrum of alkyl- and arylalkoxysilanes. The wave number of this band is characteristic of the frequency of the bond O — R of the ester group [9]. This band is shifted in the spectra of tetraphenoxysilane $(C_6H_5O)_4Si$ to 8.05 μ (1242 cm^{-1}).

Apart from the absorption band which is caused by vibration of Si — C and Si — O bonds which are specific for silico-organic compounds, other characteristic absorption bands of certain atomic groups or bonds can be observed in the infrared absorption spectra of these compounds.

In compounds containing the methyl groups linked with an aliphatic radical, bands are observed at 3.47 μ (2879 cm^{-1}), 6.9 μ (1449 cm^{-1}) and 7.24 μ (1380 cm^{-1}) [2]. The vibration frequency of the first band is a characteristic frequency of valency vibrations of the $C\begin{matrix}H\\ -H\\ H\end{matrix}$ bond, while the vibration frequencies of the other bands are characteristic frequencies of the deformation vibrations of this bond.

According to published results [10], bands, the vibration frequencies of which are characteristic for the bonds $C\begin{matrix}H\\ H\end{matrix}$ and C — H in the groups $=CH_2$ and $\equiv CH$ in aliphatic compounds $R'R''CH_2$ and $R'R''R'''CH$, are very near

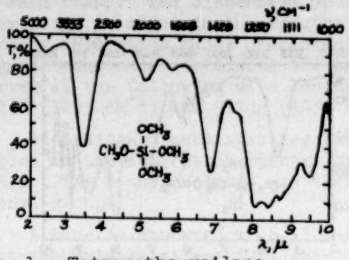

Fig. 1. Tetramethoxysilane.
3.45(2899)38; 6.85(1459)25.4; 8.05 (1242)7, 8.4(1190)7; 8.7(1149)11.5, 9.5(1053)24.

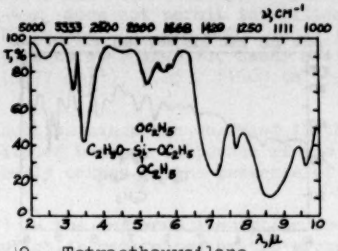

Fig. 2. Tetraethoxysilane.
3.2(3125)70, 3.45(2899)41; 7.1(1408) 23, 7.7(1299)37.4, 8.6(1163)10, 9.6(1042)28.

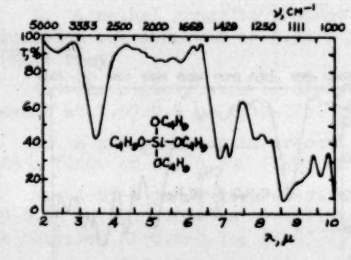

Fig. 3. Tetrabutoxysilane.
3.45(2899)42, 6.85(1459)31.2; 7.1 (1408)32.2; 7.85(1274)42.2, 8.2(1220) 41; 8.6(1163)8, 9.6(1042)21.

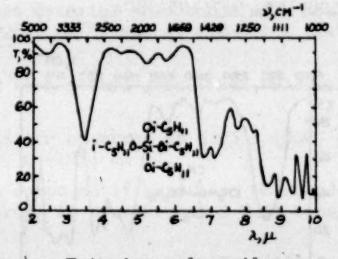

Fig. 4. Tetraisoamyloxysilane.
3.45(2899)40.4; 6.8(1471)31; 7.1 (1408)30; 7.75(1290)47; 8.2(1220) 45.5; 8.6(1163)14.5; 8.9(1124)8; 9.3(1075)10.5; 9.6(1042)7; 9.8(1020) 10.

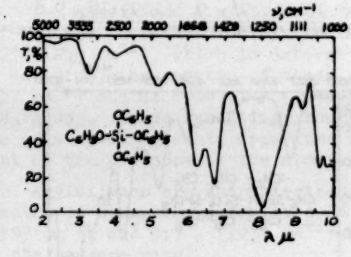

Fig. 5. Tetraphenoxysilane.
3.25(3077)78; 6.25(1600)27; 6.7(1493) 18; 8.05(1242)3; 9.1(1099)60; 9.6 (1042)26; 9.8(1020)26.4

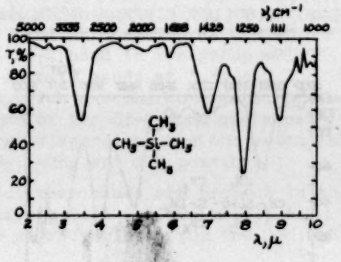

Fig. 6. Tetramethylsilane.
3.45(2899)54; 6.95(1439)57.4; 7.95 (1258)24; 8.95(1117)54; 9.5(1053) 80; 9.7(1031)83.4; 9.9(1010)85.

Figs. 1-12 represent the infrared absorption spectra of silico-organic compounds and of 25% solutions of the same compounds in carbon tetrachloride. The first number denotes the wave length in microns, while the second (in parenthesis) denotes the wave numbers characteristic of the vibration in cm^{-1}, and the third number the transmission in %.

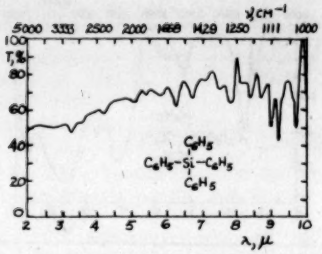

Fig. 7. Tetraphenylsilane.
3.25(3077)47; 6.25(1600)62, 6.7(1493)66; 7.5(1333)71.4; 7.8(1282)64; 8.4(1190)66.6; 8.7(1149)67; 9.0(1111)50; 9.2(1087)43, 9.7(1031)50.

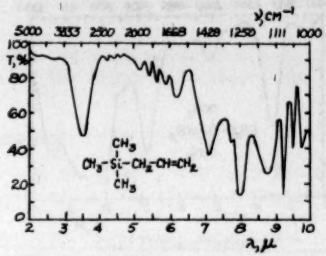

Fig. 8. Trimethylallylsilane.
3.5(2857)47; 6.15(1626)69; 7.1(1408)36; 7.7(1299)44.4; 8.0(1250)13.6; 8.75(1143)26; 9.2(1087)13; 9.5(1053)40; 9.75(1026)40.

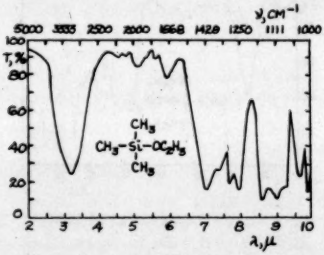

Fig. 9. Trimethylethoxysilane.
3.2(3125)24; 7.0(1429)15.4; 7.7(1299)19; 7.95(1258)15; 8.6(1163)10; 9.0(1111)10, 9.65(1036)23.5; 9.9(1010)14.

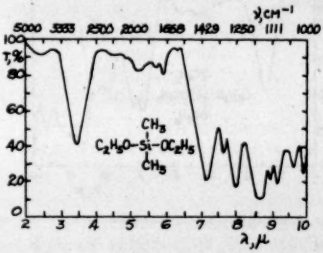

Fig. 10. Dimethyldiethoxysilane.
3.45(2899)41; 7.1(1408)20.4; 7.6(1316)6; 7.95(1258)15.2, 8.6(1163)10, 8.9(1124)21; 9.1(1099)18; 9.6(1042)28; 9.9(1010)25.

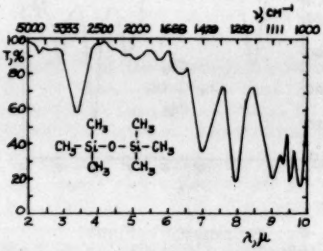

Fig. 11. Hexamethyldisiloxane.
3.4(2941)57.7; 6.95(1439)35; 7.95(1258)18.2; 9.0(1111)20; 9.3(1075)28, 9.5(1053)19, 9.8(1020)16.

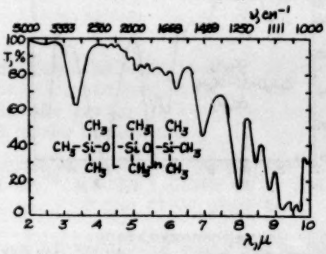

Fig. 12. Silicone oil.
3.35(2985)62, 6.2(1613)71; 6.95(14 9)45.4; 7.95(1258)16; 8.4(1190)30; 8.8(1136)14.4; 9.2(1087)3.5; 9.5(1053)3.0, 9.7(1031)2.4; 9.9(1010)30.

to each other. The dispersion of the rock salt (from which the spectrophotometer prism is made) in the spectral region 3-4 μ does not permit identification of absorption bands characteristic of the groups $=CH_2$ and $\equiv CH$. In silico-organic compounds containing the phenyl groups such as $(C_6H_5)_4Si$, bands are observed at the following wave lengths 3.25 μ (3077 cm^{-1}), 6.25 μ (1600 cm^{-1}), 6.7μ (1493 cm^{-1}) and 9.7 μ (1031 cm^{-1}).

According to published results [2], absorption bands are observed in this region in the absorption spectra of unisubstituted benzene compounds of the type C_6H_5X. The bands observed are therefore probably caused by the presence of phenyl groups.

A band is observed at 6.15 μ (1626 cm^{-1}) in the infrared absorption spectra of trimethylallylsilane $(CH_3)_3Si-CH_2-CH=CH_2$ which is determined by the groups $-CH=CH_2$. This is confirmed by the fact that an absorption band is observed just in this very region in the infrared absorption spectra of molecules containing the $-CH=CH_2$ group [2].

A summary of the results obtained is given in Table 4.

1. A methyl group is present in the test material when bands with maximum absorption are observed at 3.35-3.5 μ (2985-2857 cm^{-1}) and at 6.8-7.1 μ (1471-1408 cm^{-1}).

2. The silicon atom is directly linked to a methyl group when bands are present at 7.95-8.0 μ (1258-1250 cm^{-1}).

3. A phenyl group is present when bands are observed at 3.25 μ (3077 cm^{-1}), 6.25 μ (1600 cm^{-1}), 6.7 μ (1493 cm^{-1}) and 9.7 μ (1031 cm^{-1}).

4. A Si-O group is present in the test compound if bands are observed at 9.5-9.65 μ (1053-1036 cm^{-1}) while an ester group is present $\equiv Si-O-R$ if bands are observed at 8.6-8.7 μ (1163-1149 cm^{-1}).

5. A $-CH=CH_2$ group is present if a band is observed at 6.15 μ (1626 cm^{-1}).

These facts permit one to establish the presence of a number of atomic groupings in an unknown silico-organic compound. On the basis of these results it is possible to establish to a certain extent to what class the given silico-organic compound belongs.

1. Alkyl- and Arylsilanes. Alkylsilanes which contain the atomic group $\equiv Si-CH_3$ are characterized by the fact that a band is observed at 7.95-8.0 μ (1258-1250 cm^{-1}), which is determined by the Si-C bond in the group $\equiv Si-CH_3$. In addition, the spectra of these compounds contain bands at 3.35-3.5 μ (2985-2857 cm^{-1}) and at 6.8-7.1 μ (1471-1408 cm^{-1}),which are characteristic of the $-CH_3$ group. Bands resulting from the presence of the Si-O bond are absent. The use of a spectrographic apparatus with a large dispersion makes the establishment of the presence of the atomic group $-CH_3$, $=CH_2$ and $\equiv CH$ possible.

Arylsilanes are characterized by the fact that bands are present in the spectra of these compounds at 3.25 μ (3077 cm^{-1}), 6.25 μ (1600 cm^{-1}), 6.7 μ (1493 cm^{-1}) and 9.7 μ (1031 cm^{-1}), which are characteristic for the C-H bonds in the benzene ring.

2. Alkoxy- and Aroxysilanes. (esters of orthosilicic acid), are characterized by the presence of a band at 9.5-9.65 μ (1053-1036 cm^{-1}), in the spectra of these compounds which is determined by the Si-O bond and a band at 8.6-8.7 μ (1163-1149 cm^{-1}), which is determined by the ester group $-O-R$.

3. Alkyl- and Arylalkoxysilanes are characterized by the presence of a band at 9.5-9.65 μ (1053-1036 cm^{-1}) in the spectra and at 8.6-8.7 μ (1163-1149 cm^{-1}), which are determined by the Si-O bond and the ester group $-O-R$.

TABLE 4

Wave Numbers of the Characteristic Vibrations of Atomic Groupings and of the Most Important Bonds of the Silico-Organic Compounds Examined (Wave lengths in microns, wave numbers in cm^{-1})

Formula and designation of compound	$-CH_3$; $C\begin{smallmatrix}H\\-H\\H\end{smallmatrix}$		C_6H_5-; C—H	
	μ	cm^{-1}	μ	cm^{-1}
Tetramethoxysilane $(CH_3O)_4Si$	3.45	2899	–	–
Tetraethoxysilane $(C_2H_5O)_4Si$	3.45	2899	–	–
Tetrabutoxysilane $(n\text{-}C_4H_9O)_4Si$	3.45	2899	–	–
Tetraisoamyloxysilane $(i\text{-}C_5H_{11}O)_4Si$	3.45	2899	–	–
Tetraphenoxysilane $(C_6H_5O)_4Si$	–	–	3.25 6.25 6.7 9.7	3077 1600 1493 1031
Tetramethylsilane $(CH_3)_4Si$	3.45	2899	–	–
Tetraphenylsilane $(C_6H_5)_4Si$	–	–	3.25 6.25 6.7 9.7	3077 1600 1493 1031
Trimethylallylsilane $(CH_3)_3SiCH_2-CH=CH_2$	3.5	2857	–	–
Trimethylethoxysilane $(CH_3)_3Si(OC_2H_5)$	3.2	3125	–	–
Dimethylethoxysilane $(CH_3)_2Si(OC_2H_5)_2$	3.45	2899	–	–
Hexamethyldisiloxane $(CH_3)_3SiOSi(CH_3)_3$	3.40	2941	–	–

If these compounds contained the methyl group, bands which are determined by the Si—C bond in the group $\equiv Si-CH_3$ and by the $C\begin{smallmatrix}H\\-H\\H\end{smallmatrix}$ bond in the $-CH_3$ group should be observed.

4. Siloxanes are characterized by the appearance in their spectra of a band at 9.5 9.65 μ (1053-1036 cm^{-1}), which is determined by the Si—O bond, while the band at 8.6 8.7 μ (1163-1149 cm^{-1}), which is determined by the ester group, is absent.

The final stage in our work was the testing of a technical product, "Silicone Oil."

In the infrared absorption spectra of "Silicone Oil" the following bands were found to be present: ones with maximum absorption at 3.4 and 6.95 μ which are determined by the characteristic vibration of the methyl group, one with maximum absorption at 7.95 μ , determined by the presence of a methyl group on a silicon atom, and a band with maximum absorption at 9.5 μ which is determined by the bond between silicon and oxygen.

On the basis of the results obtained, it may be considered that the test organo-silicon compound contains the atomic groups and bonds listed above.

TABLE 4 (continued)

$-CH_3$; $C\begin{smallmatrix}H\\H\\H\end{smallmatrix}$		$\equiv Si-CH_3$; Si–C		Si–O		$-CH_2-CH=CH_2$; C=C		–O–R	
μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}
6.85	1459	–	–	9.5	1053	–	–	8.7	1149
7.1	1408	–	–	9.6	1042	–	–	8.6	1163
6.85 7.1	1459 1408	–	–	9.6	1042	–	–	8.6	1163
6.8 7.1	1471 1408	–	–	9.6	1042	–	–	8.6	1163
–	–	–	–	9.6	1042	–	–	8.05	1242
6.95	1439	7.95	1258	–	–	–	–	–	–
–	–	–	–	–	–	–	–	–	–
7.1	1408	8.0	1250	–	–	6.15	1626	–	–
7.0	1429	7.95	1258	9.65	1036	–	–	8.6	1163
7.1	1408	7.95	1258	9.6	1042	–	–	8.6	1163
6.95	1439	7.95	1258	9.5	1053	–	–	–	–

SUMMARY

1. The infrared absorption spectra of several types of silico-organic compounds have been photographed.

2. On the basis of a study of these infrared spectra, a qualitative method of analysis has been worked out for silico-organic compounds which is applicable to a large class of them, in particular:

a) alkoxy- and aroxysilanes; b) alkyl- and arylalkoxysilanes; c) alkyl and arylsilanes; d) siloxanes, etc.

3. By means of certain analytical indications, it has been found possible to establish the presence of definite atomic groupings: $-CH_3$, C_6H_5-, $-CH_2-CH=CH_2$, $\equiv Si-CH_3$, –O–R, and Si–O bonds.

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COLOR REACTIONS OF CARBAZOLE, INDOLE, PYRROLE, AND SOME OF THEIR DERIVATIVES WITH BROMONITROINDANEDIONE

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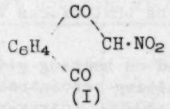
2-Nitroindanedione-1,3 (I) has already found fairly wide analytical application for the separation and identification of organic bases [1], as well as for qualitative identification of certain compounds by their color reaction with nitroindanedione [2]. One would expect that certain substituted nitroindanediones would show similar properties. It has actually been found that, e.g., a solution of carbazole in glacial acetic acid gives an intense red color with 2-bromo-2-nitroindanedione-1,3 (II). The aim of this paper is to explain the selective action and sensitivity of this reaction.



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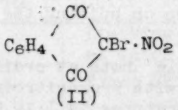

(II)

Preliminary results indicated that the intensity of the red color obtained depends partly on the concentration of carbazole, the amount of bromonitroindanedione, and the time for which the mixture is heated. It was shown that it is best to use the reagent in a dry state. Bromonitroindanedione is a colorless material; its solutions in ether, benzene, and other solvents are colorless, but its solution in glacial acetic acid is colored an intense yellow.

Increasing the amount of reagent used increases the color intensity but only up to a certain limit. Solutions boiled for 5 minutes are more intensely colored than those boiled for only 1 minute. A longer period of boiling does not lead to a further increase in intensity. The limiting concentration at which a weak rose color can still be observed is 1:500,000.

On calculating the molecular ratios, it was shown that a color can develop even when only 1 mole of bromonitroindanedione is used for 250 moles carbazole. At high dilutions a small excess of bromonitroindanedione slightly increases the color intensity, which is greatest when 2-4 moles of bromonitroindanedione are used for 1 mole carbazole. It is only when the number of moles of reagent per mole carbazole becomes greater than 8 that the sensitivity of the reaction begins to decrease.

Other solvents were tried in addition to glacial acetic acid; these included acetone, ether, dioxane, benzene, toluene, chloroform, carbontetrachloride, pyridine, methyl-, ethyl-, and isoamyl alcohols. It was only in the latter instance that a red color was obtained, but it was shown that isoamyl alcohol itself gives a red color with bromonitroindanedione. Whether or not

this is a property of isoamyl alcohol itself or of some other compound contained in it has not yet been determined. The effect of other compounds on the appearance of a color was also studied. It was found that the presence of the following organic compounds did not interfere with the color; formic, tartaric, benzoic, cinnamic, phthalic, picric, and other acids; acetophenone, benzophenone, anthraquinone, phloroglucinol, naphthalene, acetamide, acetanilide, glycerol, etc. A number of other compounds, however, interfere with the development of a red color, and only a yellow-colored solution is obtained. These compounds included phenol, pyrocatechol, resorcinol, hydroquinone, salicylic, oxalic and anthranilic acids, aniline, o-nitraniline, diphenylamine, urea, leucine, α-naphthol, formaldehyde, etc. All these reagents are known to be easily brominated, and it is possible that the reagent is thereby destroyed because it is easily converted into the nitroindanedione.

3-Nitrocarbazole and 3,6-dinitrocarbazole tested in the same way did not give a red color with bromonitroindanedione; only yellow solutions were obtained. N-acetylated carbazole did not give any characteristic color with bromonitroindanedione either; if a little carbazole is added, the red color is obtained. This reaction may therefore be used for checking the purity of N-acyl carbazoles. Since the reaction of carbazole with bromonitroindanedione is fairly sensitive, it was of interest to check this reaction with simpler analogs; i.e., with indole and its derivatives.

Indole gave a red color with bromonitroindanedione, but in contrast to carbazole, the color appears without heating and becomes more intense after a few hours. The concentration limit for indole is 1:100,000.

Calculation shows that a red color appears when there is only 1 mole reagent: 350 moles indole, while for a ratio of 1 mole reagent to 7 moles indole, the solution becomes brown on boiling the solution. This means that excess reagent should be avoided.

2-Methylindole both at ordinary temperatures and on heating gives a violet-red color with bromonitroindanedione. The limiting concentration at ordinary temperatures is 1:10,000, and on heating 1:40,000 (dirty-rose color). A large excess of reagent is to be avoided here again, particularly on heating the solution acquires a brown color.

3-Methylindole in glacial acetic acid at a dilution of 1:1,000 gives a different color with bromonitroindanedione; the color is greenish after 1 hour but changes to blue on standing for a day. On heating, the following sequence of color changes occurs: red, red-violet, blue-violet, blue. All these changes occur in the course of 1 minute. The limiting concentration at which 3-methylindole can be detected is 1:4,000. When excess reagent is used, only an orange-yellow color is obtained.

7-Methylindole both at ordinary temperatures and on heating gives a red color with bromonitroindanedione. Excess of reagent should be avoided. Heating increases the reaction sensitivity slightly. Limiting concentration 1:40,000.

2,3-Diphenylindole gives a violet-red color under the conditions indicated. Limiting concentration 1:100,000.

Heteroauxin only gives a red color after prolonged heating. Limiting concentration 1:1,000. It is possible that heteroauxin itself does not give a positive reaction, but on heating decomposes to form indole or 3-methylindole, which reacts with the bromonitroindanedione.

Tryptophane in glacial acetic acid gives a rose color with a brownish-green fluorescence on reacting with bromonitroindanedione, while a small amount of black precipitate is formed. Excess reagent changes the color to reddish-brown and destroys the fluorescence. Limiting concentration 1:100,000.

The following amino acids were tested in parallel: glycine, α-alanine, α-aminobutyric acid, leucine, and histidine hydrochloride. All of them in glacial acetic acid give a yellow color. It can be assumed therefore that this reaction is specific for tryptophane and is more sensitive than the Miller-Lyons reaction with phenol and sodium hypochlorite or with sodium hypochlorite and hydrochloric acid [3], the sensitivity of which, according to the author, is 1:31,900.

Finally, the basic compound of this group of heterocyclics was tested, viz., pyrrole itself; this gives a reddish-violet color on heating with bromonitroindanedione in glacial acetic acid. Limiting concentration 1:10,000.

Many other nitrogen containing heterocyclic compounds which were tested only give a yellow color in glacial acetic acid on testing with bromonitroindanedione, e.g., pyridine, α-picoline, 2,4-dimethylpyridine, piperidine, conine, nicotine, quinoline, isoquinoline, benzimidazole, 3,5-dimethylpyrazole, antipyrine, caffeine, xanthine, etc.

The reaction is carried out as follows: The test material is dissolved or suspended in glacial acetic acid, a little bromonitroindanedione is added, and the mixture allowed to stand for some time or heated for a few minutes. A characteristic color is obtained in the presence of many compounds with the pyrrole ring (see table). Carbazole and heteroauxin only give a color after heating the solution; the rest give a color without heating. Heating accelerates the appearance of color and makes the reaction somewhat more sensitive. Pyrrole only gives a dirty green color without heating.

TABLE

Colors Obtained with Bromonitroindanedione in Glacial Acetic Acid

Compound	Color of solution	Limiting concentration at which a color is still observable
Carbazole	Red	1:500,000
Indole	Red	1:100,000
2-Methylindole	Red-violet	1: 40,000
3-Methylindole	Blue	1: 4,000
7-Methylindole	Red	1: 40,000
2,3-Dimethylindole	Violet-red	1:100,000
Tryptophane	Rose with brownish-green or green fluorescence (and a black precipitate down to dilutions of 1:20,000)	1:100,000
Heteroauxin	Red	1: 1,000
Pyrrole	Red-violet	1: 10,000

Note. V. Petrovska carried out some of the experimental work.

SUMMARY

2-Bromo-2-nitroindanedione-1,3 gives characteristic colors with many compounds containing the pyrrole ring in glacial acetic acid. Of major importance is the reaction with carbazole, which is the most sensitive, and that with tryptophane which is especially specific, since not one of the heterocyclic compounds tested gives this reaction; no other amino acid tested gives this reaction either.

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COLOR REACTIONS OF CERTAIN MERCURIATED AROMATIC AMINES WITH NITRITES

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Certain mercuriated secondary and tertiary aromatic amines form crystalline red or yellow compounds with nitrites in glacial acetic acid solution [1]. The intensity of the color of millimolar solutions of these compounds is greater than that of the products obtained from the respective solutions of non-mercuriated amines.

This fact agrees with the chromophore theory, according to which the change-over of a colored undissociated molecule to the ionic state (formation of organo-mercury salts) leads to a more intense color [2,3].

The present paper is devoted to the study of the reaction of mercuriated aromatic amines with nitrites, and of the possibility of using organo-mercury compounds and their synthesis for the determination of nitrites and certain secondary or tertiary aromatic amines.

Monomercuriated methyl-, ethyl-, dimethyl-, diethyl- and ethylbenzylaniline were prepared for this study, the latter being prepared in a similar manner to that given for benzylaniline [4,5].

In order to compare the nitrosation reactions, we also carried out tests with the non-mercuriated compounds, in this case the secondary aromatic amines were subjected to additional purification [6].

These reactions were carried out at 85-100° in acetic acid solution, since mineral acids decompose the organo-mercury compounds [4,5], while heating increases the color intensity of the solution. There are indications in the literature [7], of similar reactions being carried out at 40-80°.

In order to evaluate the effect of mercuriation on the intensity of the colors obtained, some of the nitrosated product was obtained as follows.

To a solution of the organo-mercury compound in 10% and of aromatic amine in 1% acetic acid solution was added excess of sodium nitrite, and the mixture heated for 5 minutes at 85-100°. When this is done, the mercuriated compounds form crystalline products (Table 1), methylaniline – red, and dimethylaniline – a dark green oily liquid.

The nitrosation products gave blue and green colors when tested by the Lieberman reaction, thus indicating the presence of nitroso groups [7,8].

The yellow color of the solutions of the compounds obtained (at pH 4-4.5) is observable at the following concentrations, calculated in terms of the free base, for mercuriated amines – 0.35 μ g of dimethylaniline or 3.7 μg of methylaniline, while for the non-mercuriated compounds the respective values were 1.6 or 22 μ g in 5 ml of 1% acetic acid.

When the mercuriation and nitrosation reactions were combined, microgram amounts of nitrites and certain secondary and tertiary amines could be detected. These determinations were carried out by the standard series method and photometrically, in the latter method a 436 m μ light filter was used.

Determination of Nitrites. To 4 ml of an aqueous test solution was added 1 ml of reagent (10 mg/ml of the organo-mercury compound or the corresponding amount of aromatic amine in 10% acetic acid), 1 ml of 1% acetic acid and the whole heated for 5 minutes at 85-100°. On cooling, 20% sodium acetate was added at the rate of 0.1 ml per ml of 1% acetic acid. The pH was thus raised to 4-4.5. The color develops rapidly and keeps for one month. A calibration curve was drawn up in the same way, the solutions used containing from 0.1 to 20 μ g NO_2^- in 5 ml.

TABLE 1

Characteristics of the Reaction Products of Nitrous Acid with Mercuriated Aromatic Amines

Nitrosated Compound	M.p. (°C)	Reaction product		
		M.p. (°C)	Color of crystals	Color of solution in 10% acetic acid
1,4-Methylamino-phenylmercuri-acetate	149-150	128-130, decom-poses at 181-183	Pale orange needles, rods.	Greenish-yellow to orange.
1,4-Ethylamino-phenylmercuri-acetate	128-129	125-126, decom-poses at 175	Pale yellow needles, plates.	Greenish-yellow to orange.
1,4-Dimethylamino-phenylmercuri-acetate	164-165	105-107	Orange-red plates with a metallic luster.	Greenish-yellow to red.
1,4-Diethylamino-phenylmercuri-acetate	104-105	103-104	Dark red prisms with metallic luster.	Greenish-yellow to red.
1,4-Ethylbenzyl-aminophenyl-mercuriacetate.	91- 92	No crystalline precipi-tate formed.		Greenish-yellow to red.

TABLE 2

Sensitivity of the Reactions for the Colorimetric Determination of Nitrites with Mercuriated and Non-Mercuriated Aromatic Amines

Organo-mercury compounds	NO_2^- μg/5 ml	Aromatic amines	NO_2^- μ g/5 ml
1,4-Methylaminophenyl-mercuriacetate	0.7	Methylaniline	10
1,4-Ethylaminophenyl-mercuriacetate	0.9	Ethylaniline	15
1,4-Dimethylaminophenyl-mercuriacetate	0.08	Dimethylaniline	1
1,4-Diethylaminophenyl-mercuriacetate	0.16	Diethylaniline	1.5
1,4-Ethylaminophenyl-mercuriacetate	0.1	Ethylbenzylaniline	1.5

Table 2 contains results on the reaction sensitivity, while Figs. 1 and 2 illustrate the basic characteristics of the optical properties of the colored solutions. Fig. 2 shows that the color follows the Lambert-Beer law.

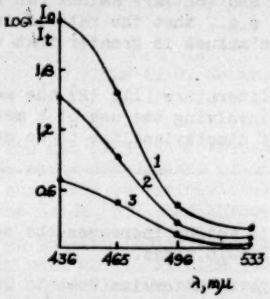

Fig. 1. Relation between light absorption and wave length for varying nitrite concentrations.
Reagent: 1,4-dimethylaminophenylacetate; 1, 2, 3, respectively at 20, 13, 6.5 μ g NO_2^-

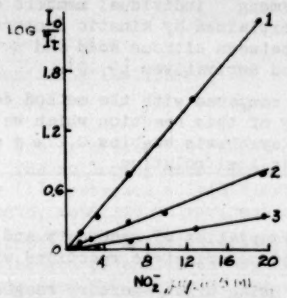

Fig. 2. Relation between color intensity at λ = 436 m μ and nitrite concentration.
1 – With 1,4-dimethylaminophenylmercuriacetate, 2 – with 1,4-methylaminophenylmercuriacetate, 3 – with dimethylaniline.

A large excess of halides, nitrates, sulfites, and sulfates, and a 25-fold excess of H_2S water has no effect on the color.

By using this reaction in reverse it is also possible to determine 1 μ g of mercuriated tertiary-, or down to 10 μ g of secondary aromatic amine in 5 ml solution.

Determination of Aromatic Amines. To 4 ml of aromatic amine solution was added 0.1 ml of mercuric acetate (15 mg/ml) solution in 1% acetic acid. A blank test was put on at the same time, no mercuric acetate being added in this case. The solution was heated for 5 minutes at 85-100°, 0.1 ml of 1% sodium nitrite was added, and the whole heated for another 5 minutes. On cooling, 0.4 ml of 20% sodium acetate was added, the solution was then mixed and determined colorimetrically. The standards used were prepared in exactly the same way, 0.5 to 25 μ g of tertiary or 4 to 20 μ g of secondary aromatic amine in 5 ml acetic acid being used. Results of reaction sensitivity are given in Table 3.

TABLE 3

Sensitivity for the Colorimetric Determination of Aromatic Amines by Means of Nitrites

Amine	μ g amine in 5 ml solution	
	With mercurization	Without mercurization
Methylaniline	4	20
Ethylaniline	5	25
Dimethylaniline	0.5	1.2
Diethylaniline	0.7	1.8
Ethylbenzylaniline	0.5	1.4

Aniline, alcohol, acetone, and a 5-10 fold excess of phenol do not interfere.

These reactions can also be used for the determination of nitrites in the absence of organomercury reagents. A solution of 20 mg mercuric acetate + 6 mg of dimethylaniline in 1 ml of 1% acetic acid heated beforehand to 85-100° can be used as a reagent. The reaction sensitivity is the same as for the organo-mercury reagents (Table 2).

These tables and figures show that mercuriation effectively increases the color intensity of the solutions during reactions between aromatic amines and nitrous acid. The greater sensitivity of the reaction with tertiary amines as compared with secondary amines can be explained by the difference in position of the chromophoric group (probably NO). Small differences in reaction sensitivity among individual members of the secondary and tertiary amines can be partly explained by kinetic factors. It is known, e.g., that the rate of interaction between nitrous acid and methylated aromatic amines is greater than with ethylated derivatives [9,10].

As compared with the method described in the literature [11, 12] the sensitivity of this reaction which we have suggested involving the use of a metallo-organic synthesis enables 0.1 μg as again 1 μg of dimethylaniline to be detected in 1 ml solution.

SUMMARY

Mercuriation of secondary and tertiary aromatic amines increases the sensitivity of colorimetric reactions with nitrites by 2.5-16 times.

By using organo-mercury reagents it is possible to determine down to 0.08 μg of NO_2^-, while using the metallo-organic synthesis, down to 0.5 μg of tertiary or 4 μg of secondary aromatic amines can be determined in 5 ml solution.

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ABSORPTION OF SULFUR OXIDES BY METAL OXIDES AND SILICATES

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The use of solid absorbents for taking up sulfur oxides was fairly common in the early development of organic analysis. The following absorbents have been suggested at various times: cupric oxide [1], asbestos + lead dioxide [2], calcium oxide [3], lead chromate, silver vanadate, metallic silver, and others.

At present, solid absorbents, with the exception of metallic silver, are hardly used at all for the quantitative determination of sulfur in organic materials. Lead dioxide and lead chromate are often used for taking up the sulfur in carbon-hydrogen estimations.

Numerous papers have been devoted to the application of metallic silver for absorption of sulfur oxides and halogens, but mainly in the field of microelemental analysis. The absorption of sulfur oxides by silver at high temperatures has been successfully used in the method developed by M. O. Korshun and N. S. Sheveleva [4], and described in a monograph [5].

Our aim was to study the possibility of replacing silver by other more readilyaccessible materials. During this study absorption of sulfur oxides by metal oxides and silicates was investigated. Sulfur is determined by the increase in weight of absorbent.

Solid absorbents can be used for the analysis of organic compounds containing not only C, H, O, and S, but C, H, O, S, and N, since at temperatures of 700-800° the gaseous reaction products contain only the indifferent oxide of nitrogen, nitric oxide, which does not react with the absorbent. Consequently it is best to keep the temperature at which the reaction between sulfur oxides and absorbent is going to occur within the limits of 700-800°. Reactions between sulfur oxides and metal oxides or silicates proceed as follows:

$$MeO + SO_3 = MeSO_4;$$

$$Na_2SiO_3 + SO_3 = Na_2SO_4 + SiO_2.$$

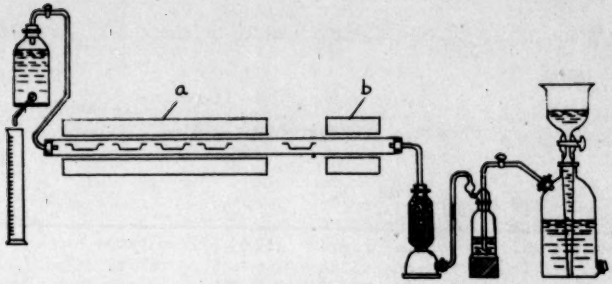
From which the conversion factor is —

$$\frac{S}{SO_3} = 0.40049 \sim 0.4005;$$

which is slightly less than the factor for silver $\frac{S}{SO_4} = 0.3338$.

Principle of the Method

Quantitative determination of sulfur in organic compounds by absorption with solid absorbents consisted in combustion of the sulfur-containing material in an empty tube at 800° in the presence of chromic oxide as a catalyst, this being sprinkled over the aliquot of test material contained in a boat. The sulfur oxides formed were absorbed at 700-800° with solid absorbents placed in boats in the combustion tube. The oxygen throughput was 50 ml/minute. Sulfur content was determined by the increase in weight of the boat. The apparatus is depicted in the diagram.



Preparation for Analysis

The absorbent was first of all calcined in a muffle at 600-800° for 3-4 hours, according to the type of absorbent used. Before analysis the absorbent was placed in a porcelain boat, which was then introduced into the combustion tube and heated for 1-2 hours in a stream of oxygen running at 50 ml/minute. The boat and contents were then removed from the tube and placed in a test tube fitted with a ground glass stopper, and the whole kept in a desiccator. The tube was allowed to cool for 20-30 minutes. The test tube was then closed and weighed.

The following oxides were tested as absorbents for sulfur oxides: magnesium oxide, cupric oxide, lead dioxide, cadmium oxide and sodium silicate.

Blank tests were carried out beforehand in order to establish the change in weight of absorbent which occurs during calcining in the tube in a stream of oxygen. The throughput was varied. The results obtained for some of the absorbents are adduced in Table 1.

These results show that an increase in oxygen throughput leads to losses in weight of the absorbent as a result of carry-over of particles as shown by the large differences in weight in the blank tests. Pressing some of the oxides leads to a decrease in this loss of weight, but does not prevent it. Optimal results were obtained in the blank tests when sodium silicate was used, presumably because its particles are heavier than those of the other absorbents tried. Changes in weight of sodium silicate during combustion of saccharose in blank tests are given in Table 2.

The variations in weight of absorbent are appreciable because of the carry-over of absorbent particles and deflagration of the compound at such a low oxygen throughput.

In order to illustrate the capacity of silicate to absorb moisture and carbon dioxide from the air, results are adduced for increases in weight of silicate on leaving it in the open air in boats.

After 2 hours	0.02 g
After 24 hours	0.08 g

Experimental Procedure

Four boats containing preliminarily calcined and weighed sodium silicate were placed in the combustion tube. The aliquot of sulfur containing material

TABLE 1

Material	Weight, in g: Before calcining	Weight, in g: After calcining	Difference	Oxygen throughput, in ml/min	Temperature, in °C
Sodium silicate	63.1184	63.1185	+0.001	50	
	63.1185	63.1180	−0.0005	50	
	69.6595	69.6595	−0.0001	50	
	69.6594	69.6594	0.0000	50	800
	70.4050	70.4042	−0.0008	75	
	70.4042	70.4052	+0.0010	75	
	81.3146	81.3140	−0.0006	75	
	81.3140	81.3134	−0.0006	75	
Cadmium oxide, pressed	84.5488	84.5440	−0.0048	50	700
	83.7120	83.7058	−0.0062	50	
Magnesium oxide, unpressed	73.7108	73.6912	−0.0196	50	800
	75.9074	75.8894	−0.0080	50	
Magnesium oxide, pressed	75.8132	75.8070	−0.0052	50	
	74.5372	74.5343	−0.0029	50	
	75.8064	75.8044	−0.0020	50	800
	74.5424	74.5372	−0.0052	50	
	74.5372	74.5347	−0.0025	50	
	75.8058	75.8020	−0.0038	50	

TABLE 2

Absorbent	Weight, in g: Before combustion	Weight, in g: After combustion	Difference	Oxygen throughput, in ml/min
Sodium silicate	72.7828	72.7844	+0.0016	50
	81.7186	81.7770	−0.0016	50
	77.6832	77.6818	−0.0014	50
	87.3109	87.3094	−0.0015	50

(0.1000-0.1500 g) also in a boat was strewn with chromic oxide and placed in the tube at a distance of 3 cm from the part of the oven heated to 700-800°. Immediately on putting the boat plus aliquot in position the second electric oven between the aliquot and purifying system was switched on; the idea of the purifying system is to prevent a reverse distillation of the test material. The oxygen from the gas-holder was passed through a purifying system containing alkali. As soon as the temperature in the little electric oven had reached 700-800°, it was moved on to a quarter of the boat + aliquot gradually, and then in the course of 10-15 minutes on to the whole of the length of the boat. The boat was heated for 5 minutes and oxygen passed for another 15 minutes in order to ensure complete removal of the gaseous products. The boat was then removed from the tube, placed in an open test tube, and left in a desiccator; the whole was cooled for 25-30 minutes and weighed.

Tests showed that cupric oxide is not a suitable absorbent for the quantitative determination of sulfur because of the low temperature at which the sulfate which is formed decomposes. Lead dioxide under the experimental conditions employed changed color from yellow to red, indicating formation of red lead,

so that this oxide is unsuitable as an absorbent also. Cadmium oxide is similarly inapplicable, since there is a considerable loss in weight during blank tests; in addition their reactivity is low.

Magnesium oxide is fairly reactive, but the drawback in this case is the large carry-over of particles with the oxygen stream, as is shown by considerable losses in weight in the blank tests.

Near quantitative results for the quantitative determination of sulfur in organic compounds were obtained with sodium silicate as absorbent; results of these determinations are given in Table 3. They indicate that sodium silicate is a potential substitute for metallic silver.

TABLE 3

Absorbent	Substance and empirical formula	Weight of aliquot, in g	Increase in weight, in g	Sulfur in % Found	Sulfur in % Calculated	Difference	Absorption temp., in °C
Na_2SiO_3	p-Toluenesulfamide $C_7H_9SO_2N$	0.1142	0.0514	18.02	18.71	−0.69	800
		0.0966	0.0465	19.27	18.71	+0.56	
	Phthalsulfothiazole $C_{16}H_{13}O_5N_3S_2$	0.1310	0.0506	15.46	15.89	−0.43	800
		0.1476	0.0509	15.43	15.89	−0.46	
	4-Sulfanilylsulfanilamide $C_{12}H_{13}O_4N_3S_2$	0.1176	0.0556	18.93	19.59	−0.66	800
		0.1278	0.0602	18.87	19.59	−0.73	
	Thiosemicarbazide CH_5N_3S	0.1168	0.1030	35.31	35.17	+0.14	800
		0.1219	0.1061	34.85	35.17	−0.32	
	Sulfosalicyclic acid $C_7H_6SO_6 \cdot 2H_2O$	0.1119	0.0367	13.13	12.61	+0.52	800
		0.1530	0.0475	12.43	12.61	−0.18	
		0.1930	0.0614	12.74	12.61	+0.13	
MgO, pressed	Ditto	0.1000	0.0290	11.61	12.61	−1.00	700
		0.1552	0.0500	12.90	12.61	+0.29	
	4-Sulfanilylsulfanilamide	0.1102	0.0510	18.53	19.59	−1.06	700

Slight deviations within the limits of 0.5% in the results for sulfur content on absorption of sulfur oxides with sodium silicate are the results of a small carry-over of absorbent with the oxygen stream. It would be natural to expect that exact quantitative results are possible if a form of absorbent apparatus is used in which the absorbent itself is in the form of a tube connected to the combustion tube. This type of absorbent apparatus would prevent the loss of particles by carry-over with the oxygen stream. We managed to prove this by carrying out some analyses in such an apparatus [4] which was given to us by the Microanalytical Laboratory of the Institute of Organic Chemistry.

The results of these tests are given in Table 4 from which it is possible to conclude that sodium silicate can be used as an absorbent instead of metallic silver in elemental analysis for quantitative absorption of sulfur oxides.

SUMMARY

1. Absorption of sulfur oxides by metal oxides and silicates has been studied.

TABLE 4

Absorbent	Sample	Weight of sample, in g	Increase in weight, in g	Sulfur, in %		Difference
				Found	Calculated	
Sodium silicate	o-Toluene sulfamide	0.1238	0.0570	18.43	18.71	−0.28
		0.1224	0.0564	18.45	18.71	−0.26
	Sulfosalicylic acid	0.1592	0.0492	12.37	12.61	−0.24
		0.1025	0.0320	12.50	12.61	−0.11
	Naphthionic acid	0.1118	0.0386	13.82	13.81	+0.01
		0.1082	0.0367	13.58	13.81	−0.23
	2-/p-Amino-benzenesulfamidopyridine	0.0731	0.0228	12.60	12.86	−0.26
		0.0952	0.0302	12.70	12.86	−0.16

2. It has been shown experimentally that metallic silver can be replaced in organic analysis by more readily accessible materials, such as metallic oxides and silicates.

3. The best results were obtained with sodium silicate which rapidly and quantitatively absorbs sulfur oxides.

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IODOMETRIC DETERMINATION OF CADMIUM

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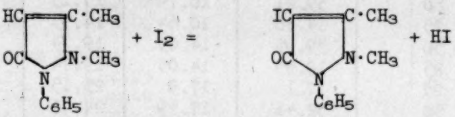
In our previous paper [1], it was shown that cadmium can be determined quantitatively by several methods including the diantipyrylorthohydroxyphenylmethane method; cadmium is also precipitated quantitatively in acid media by antipyrinebromide reagent, a compound of the following composition being obtained [2]:

$$[C_{11}H_{12}ON_2H]_2[CdBr_4]\cdot 2C_{11}H_{12}ON_2.$$

The volumetric method for the quantitative determination of antipyrine is based on the fact that it gives iodopyrine with iodine:



The residue taken in excess iodine solution is titrated with sodium thiosulfate. In view of the reversibility of the formation of iodopyrine, it is essential to add sodium acetate to take up the hydrogen iodide. Knowing how much iodine has been used for the formation of iodopyrine it is possible to calculate the amount of cadmium.

The iodometric method of determining cadmium was worked out initially on pure cadmium salts.

Cadmium solutions were prepared by dissolving 1 g metallic cadmium in nitric acid, and the solution diluted to 200 ml with water. 1 ml solution contains 5 mg cadmium. This was checked electrolytically.

EXPERIMENTAL

The antipyrinebromide reagent was prepared as follows: 10 g of potassium bromide and 5 g antipyrine were dissolved in 85 ml of 0.25 N sulfuric acid. An excess of this reagent was added to the test cadmium solution. Turbidity or a precipitate developed according to the amount of cadmium present. After rubbing with a glass rod (15-20 seconds) the precipitate rapidly changed into a crystalline form. After 30-35 seconds the precipitate was filtered through a number 4 sintered glass crucible; the filtrate was used for completely transferring all the precipitate onto the filter. The precipitate was washed once or twice with a small amount of dilute (1:1) solution of the antipyrinebromide reagent, and then, without giving it a chance to dry out, washed off the filter with 25-30 ml of water into a flask fitted with a ground-glass stopper. If the precipitate should adhere closely to the bottom of the crucible, it should be loosened first with a glass rod fitted with a rubber policeman. Tests indicated that the precipitate need not be washed with the antipyrinebromide reagent; results in this case are somewhat higher but not too high.

After the precipitate had been washed, 3 g of sodium acetate was added followed by 25-30 ml of 0.1 N iodine solution. The flask was then stoppered and the liquid thoroughly shaken; immediately or sometime after, a precipitate

was formed which appeared in the shape of dark brown colored threads. After 30-40 minutes, from 25-50 ml of ethyl alcohol was added until all the precipitate dissolved, and the excess iodine back titrated with 0.1 N sodium thiosulfate.

1 ml of 0.1 N iodine is equal to 1.405 mg cadmium.

Results of tests are adduced in Table 1.

TABLE 1

Amount of cadmium, in mg	Amount of antipyrine bromide reagent added, in ml	Amount of 0.1 N iodine added, in ml	ml of 0.1 N sodium thiosulfate used in titrating iodine	Amount of 0.1 N iodine used to form iodopyrine, in ml	Cadmium found, in mg	Absolute error, in mg
5	5	25	21.38	3.62	5.09	+0.09
10	10	50	42.87	7.13	10.02	+0.02
15	15	50	39.21	10.79	15.15	+0.15
15	15	25	14.36	10.64	14.95	-0.05
20	20	50	39.95	14.05	19.74	-0.26
20	20	25	10.95	14.05	19.74	-0.26
25	25	25	7.1	17.9	25.15	+0.15
25	25	50	32.41	17.59	24.71	-0.29
25	25	50	31.92	18.08	25.4	+0.4

The results obtained are satisfactory.

This iodometric method for cadmium was checked in the presence of other salts. Solutions of cupric chloride ($CuCl_2 \cdot 2H_2O$) and magnesium sulfate ($MgSO_4 \cdot 7H_2O$) of varying concentrations were used and known amounts of cadmium solution added to them. For each ml of the mixture thus obtained ca. 2.5-3 ml of the antipyrinebromide reagent was required for precipitation of cadmium, and in each case 25 ml of 0.1 N iodine solution was used.

The results are adduced in Table 2.

TABLE 2

Amount of cadmium, in mg	Amount of other salts, in g		Cadmium found, in mg	Absolute error, in mg
5	0.25	$CuCl_2 \cdot 2H_2O$	4.95	-0.05
5	0.25	$CuCl_2 \cdot 2H_2O$	5.06	+0.06
10	0.25	$CuCl_2 \cdot 2H_2O$	10.13	+0.13
15	0.25	$CuCl_2 \cdot 2H_2O$	14.89	-0.11
20	0.25	$CuCl_2 \cdot 2H_2O$	19.67	-0.33
25	0.25	$CuCl_2 \cdot 2H_2O$	24.38	-0.66
15	0.5	$CuCl_2 \cdot 2H_2O$	15.02	+0.02
20	0.5	$CuCl_2 \cdot 2H_2O$	19.91	-0.09
10	0.25	$MgSO_4 \cdot 7H_2O$	10.16	+0.16
15	0.25	$MgSO_4 \cdot 7H_2O$	15.02	+0.02

This method was used for the determination of cadmium in various alloys, such as Elektron, which contains magnesium, aluminum and zinc, and iron-aluminum alloy, which contains copper, iron, aluminum, zinc and manganese; in both cases the cadmium was added artificially.

ANALYTICAL PROCEDURE

1 g of Elektron was dissolved in sulfuric acid (1:10). 1 g of the bronze was dissolved in 10 ml dilute (1:1) nitric acid, and after evaporation on a water bath, 50 ml water was added. Excess antipyrinebromide reagent was added to known volumes of the solutions of these two respective alloys containing a known weight of cadmium; subsequent procedure was as outlined above.

Analytical results are given in Table 3.

TABLE 3

Amount of cadmium added, in mg	Amount of cadmium found, in mg	Absolute error, in mg
Elektron alloy		
10	10.6	+0.6
10	10.19	+0.19
15	15.17	+0.17
20	20.02	+0.02
25	24.94	−0.06
Ironaluminum bronze		
15	14.77	−0.23
20	20.44	+0.44
20	19.6	−0.4
25	24.38	−0.62

TABLE 4

Amount of cadmium taken, in mg	Amount of cadmium found, in mg	Absolute error, in mg
10	10.23	+0.23
12.5	12.25	−0.25
12.5	12.25	−0.25
15	14.61	−0.39
17.5	17.14	−0.36
20	20.18	+0.18

TABLE 5

Amount of cadmium taken, in mg	Amount of other salts, in g		Amount of cadmium found, in mg	Absolute error, in mg
10	1	$MgSO_4 \cdot 7H_2O$	9.95	−0.05
15	1	$MgSO_4 \cdot 7H_2O$	14.89	−0.11
10	0.5	$CuCl_2 \cdot 2H_2O$	9.95	−0.05
15	0.5	$CuCl_2 \cdot 2H_2O$	15.06	+0.06
5	0.25	$(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$ + 0.25 $CoCl_2 \cdot 6H_2O$	4.95	−0.05
10	0.25	$(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$ + 0.25 $CoCl_2 \cdot 6H_2O$	9.95	−0.05
15	0.25	$(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$ + 0.25 $CoCl_2 \cdot 6H_2O$	15.17	+0.17

These results show that the antipyrine bromide- iodometric method for determination of cadmium gives completely satisfactory results. The relative experimental error varies within the limits ±3%.

Further experiments showed that cadmium could be successfully determined by a saturation method.

If alkali is allowed to react with the precipitate, $[C_{11}H_{12}ON_2]_4H_2[CdBr_4]$, formed after addition of the antipyrinebromide reagent to solutions of cadmium salts, then the hydrogen ions are neutralized. The method of precipitating cadmium remains the same as during the iodometric method. The precipitates are washed from the glass crucible with 50 ml water into a 250-300 ml flask. The solution in the flask is then gently heated to dissolve all the precipitate,

the solution formed is then diluted to 150 ml with water and titrated with 0.1 N alkali in the presence of 5 drops of methyl orange. 1 ml 0.1 N NaOH corresponds to 5.62 mg cadmium. The first tests were carried out with pure cadmium salts (see Table 4).

Cadmium was subsequently determined in the presence of other salts; magnesium and nickel sulfates, copper and cobalt chlorides. Analytical results are adduced in Table 5.

Finally cadmium was determined by this method in the presence of other metals in the two alloys Elektron and Ironaluminum bronze, the cadmium itself had to be added artificially to the alloys (see Table 6).

TABLE 6

Amount of cadmium added, in mg	Amount of cadmium found, in mg	Absolute error, in mg
Elektron alloy		
10	10.12	+0.12
20	20.23	+0.23
Ironaluminum bronze		
10	9.84	−0.16
15	14.61	−0.34

These results show that the saturation method gives satisfactory results for the determination of cadmium.

SUMMARY

1. Two volumetric methods have been worked out for the determination of cadmium – an iodometric one and a neutralization method, both based on the use of antipyrinebromide reagent.

2. By means of both these methods cadmium can be determined in the presence of magnesium, copper, zinc, cobalt and other metals.

3. The relative experimental error varies within the limits ±3%.

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IODOMETRIC DETERMINATION OF ARSENIC ACID USING ORGANIC SOLVENTS

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The first stage of the reversible oxidation of iodides by arsenic acid can be expressed by the following equation:

$$H_3AsH_4 + 2I^- + 2H \rightleftharpoons H_3AsO_3 + H_2O + I_2. \quad (1)$$

This reaction has been studied by many authors [1-8] with the aim of choosing conditions such that it will go completely from left to right and can then be used for the quantitative iodometric determination of arsenic acid. It has been found that in strong acid media the equilibrium is displaced from left to right to quite an appreciable extent, but on the other hand under these conditions titration of the strong acid solution with sodium thiosulfate is not easy. Thus if the solution is diluted before titration in order to decrease the effect of the strong acid medium on the sodium thiosulfate, this will also favor the right-to-left process in reaction (1). The use of a large excess of iodide is accompanied by large errors as the result of oxidation by atmospheric oxygen. Finally it should be noted that ions of iron (III), manganese, molybdate, tungstate, and other catalysts do not, according to published results, show an appreciable effect on the reaction velocity.

The problem of a direct iodometric determination of arsenic acid thus remains open. We were particularly interested in this question as a basis for a possible arsenate method of determining many metals which are capable of forming arsenates of low solubility. On the basis of detailed investigations we succeeded in developing a method for the iodometric determination of arsenic acid in strong acid media and in the presence of a small excess of iodide, based on displacing the equilibrium in reaction (1) from left to right by extracting the iodine formed with organic solvents.

The Use of Organic Solvents in Aqueous Media with Normal pH

On the basis of equation (1) by the law of mass action:

$$\frac{[H_3AsO_4]}{[H_3AsO_3]} = \frac{[I_2]}{[H^+]^2 \cdot [I^-]^2} \cdot K \quad (2)$$

From this expression it readily follows that the ratio of the concentrations of arsenic and arsenous acids should vary in accordance with the completeness of iodine extraction by the organic solvents. According to the distribution law of iodine between the aqueous phase and organic solvent:

$$[I_{2\,\text{aqueous phase}}] = K_{\text{partition}} \times [I_{2\,\text{organic solvent}}] \quad (3)$$

Since the solubility of iodine in certain organic solvents is many times (100-1000 times) greater than that in water, then for the reduction of arsenic acid according to equation (1), it is possible to write:

$$[I_{2\,\text{organic solvent}}] \cdot V_{\text{organic solvent}} \approx [H_3AsO_3] \cdot V_{\text{aqueous phase}} \quad (4)$$

It must be remembered that according to equation (1), the total number of iodine mols formed is equal to the number of mols of arsenous acid formed.

From equation (4)

$$[I_{2\,\text{organic solvent}}] \approx \frac{[H_3AsO_3] \cdot V_{\text{aqueous phase}}}{V_{\text{organic solvent}}}$$

for

$$V_{\text{aqueous phase}} = V_{\text{organic solvent}}$$

we have

$$[I_{2\,\text{organic phase}}] = [H_3AsO_3],$$

Substituting this in equation (3), we have

$$[I_{2\,\text{aqueous phase}}] = K_{\text{partition}} [H_3AsO_3]. \quad (5)$$

Substituting the value of $[I_{2\,\text{aqueous phase}}]$ from equation (5) in equation (2), we get

$$\frac{[H_3AsO_4] \cdot [H^+]^2 \cdot [I^-]^2}{[H_3AsO_3]^2 \cdot K_{\text{partition}}} = K$$

or

$$\frac{[H_3AsO_4] \cdot [H^+]^2 \cdot [I^-]^2}{[H_3AsO_3]^2} = K \cdot K_{\text{partition}} = K_1. \quad (6)$$

Thus the use of organic solvents for removing iodine (should) changes the equilibrium constant in proportion to the value of the partition coefficient of iodine between aqueous phase and organic solvent:

$$K_1 = K \cdot K_{\text{partition}} \quad (7)$$

where K_1 – is the equilibrium constant when a given organic solvent is used; K – the equilibrium constant when no organic solvent is used; $K_{\text{partition}}$ – is the partition coefficient of iodine between water and the organic solvent used.

From calculations based on equation (7) and the respective partition coefficients of iodine [10], we compiled Table 1.

TABLE 1

Organic solvent	$K_{\text{partition}}$ Partition coefficient at 25°	Equilibrium constant when no organic solvent is used K	Equilibrium constant when organic solvent is used K_1
Carbon tetrachloride	0.0111	$7 \cdot 10^{-2}$	$7.8 \cdot 10^{-4}$
Chloroform	0.005		$3.5 \cdot 10^{-4}$
Carbon bisulfide	0.0009		$6.3 \cdot 10^{-5}$
Benzene	0.0008		$5.6 \cdot 10^{-5}$

These results show that the equilibrium constant of the reduction of arsenic acid with iodine changesby as much as 2-3 times according to the organic solvent used. This is of great importance for other similar reversible reactions.

According to extraction theory, the bigger the

volume of solvent used, the more complete the extraction. On the other hand, the use of a given amount of solvent in small portions gives much better results than one extraction with the same total volume of extraction agent. Nevertheless repeated extractions followed by a separation of the organic solvent layer each time are accompanied by certain losses which complicate the method and draw out the time of extraction. We decided therefore on one extraction without separation of the layer of organic solvent. As a consequence, in order to achieve as complete a displacement of the equilibrium as possible, we had to resort to the use of the largest possible volume of solvent.

According to equations (3) and (4):

$$[I_{2\,\text{aqueous phase}}] \approx K_{\text{partition}}[H_3AsO_3]\,\frac{V_{\text{aqueous phase}}}{V_{\text{organic solvent}}}$$

On substituting this value in equation (2), we get:

$$\frac{[H_3AsO_4]\cdot[H^+]^2\cdot[I^-]^2\cdot V_{\text{organic solvent}}}{[H_3AsO_3]\cdot V_{\text{aqueous phase}}} = K\cdot K_{\text{partition}} = K_1 \qquad (8)$$

This equation is more general than equation (6).

From equation (8) it follows that the completeness of reduction of arsenic acid to arsenous acid depends on the ratio of the volumes of organic solvent and aqueous phase.

As titration proceeds the iodine shifts from the organic solvent layer to the aqueous phase and reacts with sodium thiosulfate because the latter is insoluble in the organic solvents used.

The reaction between iodine and sodium thiosulfate is not appreciably reversible, so that a decrease in iodine concentration according to the partition coefficient of the latter between aqueous phase and the organic solvent used does not affect (or has practically no effect) on the accuracy of the titration. As titration of the iodine found in the organic solvent layer proceeds, it will pass over into the aqueous phase. When, however, a very large volume of organic solvent is used, this reverse movement of iodine into the aqueous phase will be made more difficult, so that the titration time will be longer drawn out.

Titrations in which various amounts of different solvents (chloroform, benzene, etc.) were used and a parallel series of titrations in which no solvents were used showed that organic solvents do displace the equilibrium in reaction (1) considerably, and that a volume of solvent equal to that of the aqueous phase is optimal. In macro titrations, chloroform and benzene can be used with equal success while for micro titrations (particularly at low concentrations) benzene is preferable since it is the best solvent and the most sensitive indicator.

For media 1 N with respect to acid the reaction is not complete immediately after mixing the reagents; consequently solutions with lower pH are better.

The Use of Organic Solvents at Low pH

Table 2 contains results of calculation (on the basis of equations 7 and 8) of the completeness of reduction of arsenic acid expressed by the ratio $\frac{[H_3AsO_4]}{[H_3AsO_3]}$, in relation to hydrogen ion concentration both with and without use of solvent; the respective experimental errors are also included, expressed as percentages, when working with 0.1 N solutions.

These results show that the experimental error in the tests in which no organic solvent is employed changes from 1.38 to 0.05% on changing the hydrogen ion concentration from 1 to 5.

TABLE 2

Expt. No.	$\frac{[H_3AsO_4]}{[H_3AsO_3]}$ when equilibrium is established			Error in %		
	When no organic solvent is used	When chloroform is used	When benzene is used	When no organic solvent is used	When chloroform is used	When benzene is used
1	$1.4 \cdot 10^{-2}$	$1.4 \cdot 10^{-4}$	$1.4 \cdot 10^{-5}$	1.38	0.014	0.0014
2	$3.5 \cdot 10^{-3}$	$3.5 \cdot 10^{-5}$	$3.5 \cdot 10^{-6}$	0.35	0.0035	0.00035
3	$1.56 \cdot 10^{-3}$	$1.56 \cdot 10^{-5}$	$1.56 \cdot 10^{-6}$	0.15	0.0015	0.00015
4	$9 \cdot 10^{-4}$	$9 \cdot 10^{-6}$	$9 \cdot 10^{-7}$	0.09	0.0009	0.00009
5	$5.6 \cdot 10^{-4}$	$5.6 \cdot 10^{-6}$	$5.6 \cdot 10^{-7}$	0.05	0.0005	0.00005

When chloroform was used even for 1 N media the error was only 0.014%, while at $[H^+] = 4$, the error was less than the 0.001%. When benzene was used, the error was ten times less.

We studied the effect of sulfuric acid as well as hydrochloric concentration on reaction velocity (1) when organic solvents were used. From these results it was established that in order to complete the oxidation of iodide by arsenic acid, it is essential that immediately after mixing the reagents, the solution should be at least 5 N with respect to hydrochloric acid and 8 N sulfuric acid.

A further series of experiments, the results of which are not adduced for reasons of space, established that when these concentrations of the respective acids are used, results which are in good agreement with each other are only obtained when titration is carried out strictly dropwise. If large amounts of thiosulfate are added, decomposition of the latter occurs in the strong acid media. As a result the solution is diluted before titration after completion of oxidation of iodide by arsenate. This permits rapid titration which obviates decomposition of the sodium thiosulfate, while the reverse reaction of equation (1) is not observed because of the extraction of iodine by the solvent. It is sufficient to dilute to 3 N hydrochloric acid or 4 N sulfuric acid by addition of an equal volume of distilled water.

The Effect of the Amount of Potassium Iodide Used

The iodine which is evolved during reaction (1) reacts with excess potassium iodide as follows:

$$I_2 + KI \rightleftharpoons KI_3$$

or in ionic form

$$I_2 + I^- \rightleftharpoons I_3^- \qquad (9)$$

By combining equations (1) and (9), we get:

$$H_3AsO_4 + 2H^+ + 3I^- \rightleftharpoons H_3AsO_3 + H_2O + I_3^- \qquad (10)$$

Iodine dissolves as molecules of I_2 in the organic solvents we used, while the iodide and triiodide do not dissolve in these solvents. Accordingly the equilibrium in equation (9) is displaced to the left.

The extent of this displacement depends on the completeness of extraction of iodine, i.e., on the partition coefficient of iodine between aqueous phase and organic solvent. The partition coefficient in turn depends on iodide concentration. At low concentrations, and when such solvents as benzene, carbon bisulfide, chloroform, etc., are used, this equilibrium is almost completely displaced to the left. We are of the opinion therefore that when organic sol-

vents are used, the reduction of arsenic acid by iodide is more correctly expressed by equation (1). It follows from this that a displacement of equilibrium to the side of the reduction of arsenic acid when working without organic solvents is proportional to the third power of the iodide concentration, while when solvents are used, it is proportional to the second power of this concentration. [See equations (1) and (10).]

It must be emphasized that when organic solvents are used in order to displace the equilibrium (1) an increase in iodide concentration will hinder a more complete extraction of iodine from the aqueous phase and consequently interfere with the displacement of equilibrium by the solvent.

In view of this the addition of the normally recommended large excess of iodide loses its point when organic solvents are used. On the contrary it is essential that the least possible excess of iodide be used (even more so in that addition of a large excess of iodide leads to additional errors and to results which do not agree with each other as a result of the instability of potassium iodide). This fact considerably enhances the value of the use of organic solvents.

On the other hand, the use of excess iodide is significant for speeding up reaction (1). In this connection we carried out some tests on the variation of reaction velocity with iodide concentration, while chloroform was used in sulfuric acid as well as in hydrochloric acid media. It was thereby established that the optimal amount of iodide should be a twofold excess in comparison with the stoichiometrically calculated amount.

An Iodometric Determination of Arsenic Acid Using Organic Solvents

To 10 ml of test solution contained in a 150-200 ml Erlenmeyer flask was added 10-12 ml of sulfuric acid (1:1) or an equivalent concentration of hydrochloric acid. To the mixture obtained was added an equal volume of chloroform or benzene (20 ml) and 3 ml of a 1.0 N solution of potassium iodide. When working with solutions of arsenate of greater strength than 0.1 N, the concentration of potassium iodide should be increased accordingly. The mixture is shaken for a few seconds in order to extract the iodine with the layer of organic solvent and to complete the reaction, an equal volume of water is then added and the solution titrated with sodium thiosulfate. At the end point when the layer of solvent has attained a weak rose color it is necessary to shake the mixture for a few seconds after the addition of each drop of thiosulfate.

Since the effect of oxidation by atmospheric oxygen becomes rather pronounced during micro titrations, carbon dioxide should be used to expel the air. Carbon dioxide is passed for ca. 1 minute into the flask over the surface of the solution before adding potassium iodide.

Results of macro- and micro-titrations are given in Table 3.

Titration in hydrochloric acid gives results which are just as accurate and reproducible as in sulfuric acid. Micro-titrations gave good results at arsenate concentrations down to 0.001 N. At lower concentrations good results can still be obtained if a blank is carried out and the air is carefully removed by passing carbon dioxide after addition of each reagent, and repeatedly passing it during the actual titration.

TABLE 3

Conc. of arsenate solution	Volume, in ml			Volume, in ml, conc. in N of potassium iodide solution	Volume, in ml of water for dilution	Amount of thiosulfate solution used in ml	Theoretical amount of thiosulfate used in ml	Deviation, in ml
	Arsenate	Sulfuric acid 1:1	Solvent					
0.2	10	10	20	3 ml 2 N	20	9.95	9.98	0.03
0.1	5	5	10	1.5 1	10	5.15	5.12	0.03
0.1	10	10	20	3 1	20	10.15	10.24	0.01
0.1	15	15	30	4.5 1	30	15.35	15.36	0.01
0.1	25	25	50	7.5 1	50	25.55	25.60	0.05
0.05	10	10	20	3 1	20	10.05	10.04	0.01
0.02	10	10	20	3 1	20	10.45	10.43	0.02
0.01	1.000	1.0	2.0	0.3 1	2.0	1.030	1.028	0.002
0.01	1.000	1.0	2.0	0.3 1	2.0	1.025	1.028	0.003
0.005	1.000	1.0	2.0	0.3 1	2.0	0.990	0.992	0.002
0.005	1.000	1.0	2.0	0.3 1	2.0	1.000	0.992	0.008
0.001	1.000	1.0	2.0	0.3 1	2.0	1.150	1.139	0.011
0.001	1.000	1.0	2.0	0.3 1	2.0	1.135	1.139	0.004
0.0001	5.000	5.0	10	1.5 1	10	0.520	0.515	0.005
0.0001	5.000	5.0	10	1.5 1	10	0.530	0.515	0.015

SUMMARY

Macro- and micro-methods have been developed for the accurate and direct iodometric determination of arsenic acid based on the displacement of the reaction equilibrium by using organic solvents to remove iodine.

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QUANTITATIVE DETERMINATION OF SODIUM AS ANTIMONATE

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Among the methods of determining sodium as antimonate mention should be made of that proposed by Vinogradov and Dundur [1], by means of which sodium can be determined if the ratio of KCl:NaCl is not greater than 2:1. In order to remove excess KCl the authors adopted the original method of treating the mixture of KCl and NaCl with ethyl alcohol; when this was done, they got a ratio of KCl:NaCl equal to 1:1 in the sodium enriched solution. In order to get such a ratio for these salts, it is ssential that the amount of NaCl in the test mixture should be ca. 0.1 g.

The aim of the work described below was to work out a similar micro method by means of which it would be possible to determine one tenth of a milligram of sodium in natural products, e.g., in plants, in the presence of large amounts of potassium.

Conditions for the Formation of Large Crystals

Previous authors [1,3,4] precipitated sodium as antimonate as follows:

To the test aqueous solution of the alkaline metals was added an aqueous neutral or alkaline solution of potassium antimonate followed by 96% ethyl alcohol to secure a more complete precipitation of sodium. When this is done, as Vinogradov and Dundur pointed out, exceedingly fine crystals are obtained which can pass through a filter, and therefore complicate filtration. When this method of precipitating sodium is employed, at the moment when the alcohol comes into contact with the mixture of solution, not only formation of a fine precipitate occurs as a result of local supersaturation, but at certain ratios of KCl, $KSb(OH)_6$, and alcohol, precipitation of reagent also occurs.

On the basis of tests connected with the crystallization process of $NaSb(OH)_6$, we established that in order to form a coarse, rapidly settling precipitate, it is essential to prepare an alcoholic solution of reagent and add it to an alcoholic solution of the mixture of NaCl and KCl. This should be carried out at 0° for 30-60 minutes in order to ensure complete precipitation of sodium.

The Optimal Concentration of $KSb(OH)_3$ in the Original Solutions

There does not seem to be unanimous agreement in the literature as to the composition of solutions of $KSb(OH)_6$ used for quantitative precipitation of sodium. Vinogradov and Dundur showed that a freshly prepared saturated aqueous solution contained 4.34 g/liter of $K_2H_2Sb_2O_7$ or calculated as $2 \cdot KSb(OH)_6$ – 5.24 g/liter. According to Prikhodko's results [2], 2 ml of a saturated aqueous solution of potassium antimonate precipitates 2.97 mg sodium. If it is assumed that the $Sb(OH)_6^-$ ion is precipitated quantitatively as $NaSb(OH)_6$, then the concentration of $KSb(OH)_6$ should be 16.97 g/liter. Other authors [4] recommend that the solution prepared should contain not less than 10 g/liter of $KSb(OH)_6$.

Concentrated aqueous solutions of $KSb(OH)_6$ (20 g/liter) are unstable, become turbid, and an amorphous precipitate is formed. Addition of KOH slows down the decomposition of the reagent, but in the course of several days a crystalline precipitate is formed in addition to the amorphous one. Dilute alkaline solutions can be kept for a longer time, but their use for precipitating sodium followed by addition of alcohol leads to a number of complications.

For a constant alcohol concentration, e.g. 25-30%, the solubility of $KSb(OH)_6$ decreases with increasing KOH, while the sensitivity of the reagent solution decreases. As a result it is essential to avoid a large excess of KOH. It is sufficient to add 0.3-0.5 g/liter of KOH to the solution of antimonate to suppress its hydrolysis.

If one takes into account the decrease in concentration of $KSb(OH)_6$ as a result of dilution on adding the reagent to a solution of alkaline salts (1 ml test solution + 4-5 ml reagent), then the following solution may be recommended for determining small amounts of sodium in the presence of 40-50 mg KCl: for the determination of sodium in a 25% alcoholic medium[1], 4.5-4.6 g/liter of $KSb(OH)_6$, 0.3-0.5 g/liter of KOH, 25-26% ethyl alcohol (Reagent 1); for the precipitation of sodium in 30% alcoholic media, 2.7-2.8 g/liter $KSb(OH)_6$, 31-32% ethyl alcohol and approximately 0.3 g/liter KOH (Reagent 2). These solutions of $KSb(OH)_6$ do not hydrolyze and can be kept for a long time.

Quantitative Determination of Sodium in Chemically Pure NaCl and in Mixtures with KCl

Determination of sodium was carried out in centrifuge tubes, well cooled in melting ice, using an iodometric end point. The aliquots of test solution in all cases were 1 ml and consisted of an alcoholic solution of NaCl or of NaCl mixed with KCl. 4-10 ml of precipitant was added to these aliquots, the amount added depending on the amount of sodium present.

Determination of sodium in solutions of chemically pure NaCl by means of the solutions of potassium antimonate recommended above in either 25 or 30% alcoholic media does not present any difficulties. The maximal experimental error in determining 0.1-1.0 mg of sodium does not exceed 6%; the mean arithmetic error is ±3%.

Best results are obtained on precipitating sodium in the presence of KCl with Reagent 1 [4.5-4.6 g/liter $KSb(OH)_6$] when the total concentration of alcohol (salt solution + reagent) is within the limits 24-25%. The salt solution NaCl + KCl should contain 20% alcohol.

Repeatable results are obtained for 0.4 mg sodium. Low concentrations of sodium (less than 0.3 mg) are not precipitated completely in the presence of KCl. Vigorous rubbing of the test tube walls with a glass rod and prolonged cooling can sometimes effect precipitation of $KSb(OH)_6$ as needles even when sodium precipitation is incomplete.

Results of determination of sodium in 29-30% alcoholic media with Reagent 2 are given in Table 2.

The minimal amount of sodium which can be determined in the presence of 40 mg KCl in 29-30% alcoholic media is 0.2 mg. The relative error does not exceed 5%.

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1) Alcohol concentration is expressed in % by volume without taking contraction on mixing into consideration.

TABLE 1

Determination of Sodium in the Presence of Potassium Chloride in 24-25% Alcohol in Water

Amount taken, in mg		K:Na	Amount of reagent, in ml	Sodium found		Mean value, in %
Sodium	KCl			in mg	in %	
0.1	40	209.8	5	0.07	70.0	115.0
	40		5	0.16	160.0	
0.2	40	104.9	5	0.135	67.5	78.3
	40		5	0.178	89.0	
0.3	40	69.9	5	0.316	105.3	100.8
	40		5	0.289	96.3	
0.4	40	52.3	5	0.412	103.0	103.8
	40		5	0.418	104.5	
0.5	40	42.0	5	0.499	99.8	101.6
	40		5	0.517	103.4	
2.0	40	10.5	10	1.990	99.5	99.5
3.0	40	7.0	10	2.956	98.5	98.5

TABLE 2

Determination of Sodium in 29-30% Alcoholic Media in Mixtures with KCl

Amount taken, in mg		K:Na	Amount of reagent, in ml	Sodium found		Mean value, in %
Sodium	KCl			in mg	in %	
0.1	40	209.8	4	0.170	170.0	
			4	0.076	76.0	123.0
0.2	40	104.9	4	0.209	104.5	
			4	0.209	104.5	104.5
0.3	40	69.9	4	0.309	103.0	
			4	0.298	99.3	101.2
0.4	40	52.5	5	0.409	102.3	
			5	0.420	105.0	103.7
0.5	40	42.0	5	0.510	102.0	
			5	0.500	100.0	101.0
1.0	40	21.0	7	0.999	99.9	
			7	0.988	98.8	99.4

Determination of Sodium in Natural Products

A solution of $KSb(OH)_6$ gives precipitates with almost all cations with the exception of potassium and small amounts of NH_4^+; for determination of sodium in natural products therefore, it is necessary to separate total chlorides without contamination from other elements.

We carried out sodium determinations in plants, water, in stomach secretions and in waste from food processing factories. Experiment showed that the mixture of sodium and potassium chlorides separated usually contained a small amount of alkaline-earth metals and magnesium. These contaminants at low sodium

concentrations in the mixtures give a turbidity with potassium antimonate and an amorphous precipitate is formed[1].

For complete removal of these interfering elements, a mixture of the following composition was used:

Water	72 ml
Saturated solution of ammonium carbonate in ammonia[2]	2 ml (no more)
10% Ammonia	5 ml
2% Alcoholic solution of o-hydroxyquinoline	5 ml
Ethyl alcohol	16 ml

When the sodium and potassium chlorides have been dissolved in the ammonia-hydroxyquinoline solution described, the solution is transferred to a centrifuge tube, and the whole heated to 60°. After cooling, the precipitate formed is centrifuged and the sodium can be determined in the transparent solution. Control tests on sodium mixed with KCl solution containing o-hydroxyquinoline, ammonium carbonate and ammonia at the same concentrations as in the mixtures adduced above gave results of the same accuracy as for determination of sodium in alcoholic solutions of NaCl + KCl.

It is thus possible to determine sodium quantitatively in the presence of 40 mg KCl in ammonia-hydroxyquinoline media in 12-15 ml centrifuge tubes: in 24-25% alcoholic media; 0.4-3.5 mg, in 29-30% alcoholic media, 0.2-1.5 mg. In the first case the maximal ratio of K:Na is 52, while in the second case it is 105.

Determination of Sodium

1. Alcoholic Solution of Potassium Antimonate. The commercial product often contains various contaminants: nitrates, free alkali, etc. In the presence of these contaminants, it is very difficult to establish the concentration of $KSb(OH)_6$ in solution by iodometric titration. Purification of the commercial product is therefore essential.

To 30-40 g of $KSb(OH)_6$ is added 100 ml distilled water (10-15°) and the whole thoroughly stirred 3-4 times in the course of 20-30 minutes. The precipitate is washed twice with cold distilled water, the water being removed by decantation. It is then washed two or three times more with distilled water under suction. The purified preparation is then dried between filter papers.

500 ml of distilled water is heated in a 1000 ml Pyrex flask to the boiling point, when 3.5 g of purified $KSb(OH)_6$ is added in small amounts and the mixture boiled for 3-4 minutes (no more). The flask is cooled under the tap and 3.5-4 ml of 10% KOH added. 185 ml of 96% ethyl alcohol is then gradually added with stirring. After 24 hours the mixture is cooled for 2-3 hours in melting ice, and the precipitate filtered through an ashless filter paper under suction. The concentration of $KSb(OH)_6$ in solution is checked by iodometric titration in a strongly acid medium (10-15% HCl). Calculations are based on the following equations:

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1) Magnesium gives a crystalline precipitate.

2) This solution is prepared by passing CO_2 generated from a Kipp through some wash water into a cooled ammonia solution until insoluble crystals form.

$$KSb(OH)_6 + 6HCl + 2KI = 3KCl + SbCl_3 + I_2 + 6H_2O;$$

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$

2-3 ml of $KSb(OH)_6$ solution are used for titration.

If the $KSb(OH)_6$ concentration is greater than 4.5-4.6 g/liter, the solution is diluted with 25.5% alcohol.

In order to determine sodium in a 30% alcoholic medium the reagent should contain 31-32% alcohol, 2.7-2.8 g/liter $KSb(OH)_6$ and ca. 0.3 g/liter KOH. A solution of this concentration is prepared by dilution of the concentrated solution. Solutions of potassium antimonate should be stored in a pyrex flask or in a flask coated with paraffin wax.

2. Concentrated HCl. Hydrochloric acid almost invariably leads to separation of traces of iodine during iodometric titration (because of its free chlorine content).

This separation of iodine can be prevented by addition of the requisite amount of sodium thiosulfate to the hydrochloric acid. 10 ml of water is added to each 100 ml of the concentrated hydrochloric acid prepared for iodometric titration and the solution thus obtained used for dissolving the precipitate.

Analytical Procedure. The chlorides of the alkali metals, separated by any suitable method, at a ratio of K:Na $\leq$ 100, are dissolved in the exact volume of freshly prepared ammonia-hydroxyquinoline mixture (see above) so that the total amount of salts does not exceed 40-45 mg/ml and the amount of sodium should be within the limits of 0.2-3.5 mg. The beaker or flask used should be covered to decrease evaporation of solvent.

The salt solution is poured into dry test tubes, which are stoppered with corks and stood for 5-10 minutes in a warm water bath (50-60°). They are then stood for 1 hour at room temperature before centrifuging. The transparent filtrate which has a yellow tinge (excess of o-hydroxyquinoline) is poured into some more dry test tubes which are stoppered with rubber bungs, and left to stand in the dark until aliquots are taken for sodium determinations. Decomposition of o-hydroxyquinoline on keeping the solution of salt mixture for several days has no effect on the analytical results.

1 ml aliquots of the ammonia-hydroxyquinoline solution of the mixture of NaCl + KCl are transferred to centrifuge tubes and in accordance with the amount of sodium taken, dilute or concentrated reagent is added. For amounts of sodium equal to 0.5-3.5 mg, initially 5 ml of concentrated reagent solution is added (T = 4.6 g/liter) and then after 10-15 minutes, according to the amount of precipitate, another 2-5 ml of the reagent is added, etc. To test tubes containing small amounts of sodium (0.2-0.6 mg) initially only 4 ml of dilute reagent (T = 2.8 g/liter) is added, and then after 10-15 minutes, according to the amount of precipitate formed, 1-3 ml is added. No reagents are added to tubes in which there is no precipitate, or it is doubtful that any has formed.

If the amount of sodium is not known, then a qualitative determination is carried out first. In order to do this, the following procedure is adopted: 4-5 ml of concentrated reagent is added to 1 ml of the test solution which is then kept under observation for 3-5 minutes. If an appreciable amount of precipitate forms, then subsequent determination of sodium should be carried out in a 25% alcoholic solution with the concentrated reagent. If no precipitate forms, or only an inappreciable amount, then the dilute reagent is used (T = 2.8 g/liter). As soon as reagent has been added, the test tubes are stood for 3-4 minutes in melting ice or snow for a preliminary cooling, the contents of the test tubes are thoroughly mixed with a glass road, the rod is grazed slightly on the sides of the tube and rinsed with 4-5 drops of 35% alcohol, and the tube left to stand for a further hour in the ice.

Preliminary cooling is essential in order to get coarse crystals of $NaSb(OH)_6$. Rapid cooling when there is a relatively large amount of sodium present leads to the formation of fine crystals.

While the test tubes are being cooled in ice, the 35% alcohol solution to be used for washing is also cooled in the same way. After an hour the precipitate which is not firmly attached to the test tube walls is displaced by means of a glass rod and centrifuged. The liquid + precipitate are sucked off with a bulb pipet. If crystals appear in the liquid then they are centrifuged out once again, etc. After removal of reagent, test tube and precipitate are stood in the ice bath.

The precipitate is washed with cooled 35% alcohol. The total volume of wash liquor for the first washing should be 1-2 ml. The tubes are centrifuged for 1-2 minutes. The wash liquor is sucked off, the test tubes cooled, and the precipitate washed again twice. The last two washings should be made with a smaller volume of 35% alcohol. The temperature of the wash liquor should not be greater than 2°.

The washed precipitate is dissolved in 6 ml of the special concentrated hydrochloric acid which does not liberate iodine. The solution is transferred to a narrow necked 50-100 ml conical flask, the test tube is rinsed 3 times with pure distilled water (3 ml of water each time), 1 ml of freshly prepared 10% potassium iodide solution is then added, and after 3 minutes, the whole is titrated with 0.025 N thiosulfate solution from a micro-buret to a weak yellow color. 1-2 drops of 0.5% starch solution is added, and the titration finished off.

For a ratio of K:Na > 100, excess KCl is preliminarily removed from the mixture of NaCl and KCl. This operation was carried out by a modification of Vinogradov and Dundur's method [1].

The mixture of NaCl and KCl is dissolved in 2 ml water and transferred to a 25 ml standard flask. The flask or beaker containing the original dry salts is rinsed first with 1 ml water to which has been added 3-4 ml of 96% ethyl alcohol, and then with alcohol only a few times. The solution is shaken and after cooling to 20°, the volume is made up to the mark with alcohol. It is then allowed to stand for 1 hour. The alcoholic solution is centrifuged and the centrifugate poured into a dry test tube (flask) from which exactly 15-20 ml of solution is taken and evaporated to dryness. The dry residue is dissolved in an exactly measured volume of the ammonia-hydroxyquinoline mixture, and further operations carried out as described above.

If during separation of excess KCl in the 25 ml flask, a large amount of precipitate is formed, then a correction for the volume of precipitate must be applied. It can be taken as a rough approximation that 1 g of precipitate has a volume of 0.5 ml; the amount of NaCl + KCl in alcoholic solution is 0.120-0.150 g. 0.15 g is therefore subtracted from the total chlorides, and the remainder divided by 2. The results obtained are the volume of precipitate which is subtracted from 25 ml.

For a ratio of K:Na $\leq$100, sodium can be determined in the presence of other salts (not chlorides) as long as all the cations with the exception of potassium and sodium are removed. In such a case the solubility of the dry salts should be sufficient for getting them into solution on treatment with ammonia-hydroxyquinoline mixture.

E.g., determination of sodium can be carried out as follows: The dry residue obtained from a definite volume of water is treated simultaneously with solutions of ammonia, ammonium carbonate, and o-hydroxyquinoline. The filtrate is evaporated to dryness after removal of the precipitate, the residue is calcined at 500° (for removal of ammonium salts) and then dissolved in the ammonia-hydroxyquinoline mixture. Subsequent procedure is the same as for determination of sodium in chloride salts.

If only the ammonia-hydroxyquinoline mixture need be used for removal of contaminants contained in the dry residue from the water, then there is no need to carry out a preliminary treatment of the dry salts.

SUMMARY

1. By means of a micro method which has been developed, it is possible to determine sodium as antimonate in the presence of large amounts of potassium.

Determination of sodium in 24-25% alcoholic media is accurate enough for a ratio of K:Na $\leq$ 50.

When 30% alcoholic media are used, it is possible to determine sodium at a ratio of K:Na of $\leq$ 100.

For a ratio of K:Na > 100 it is possible to remove excess KCl with ethyl alcohol.

The mean arithmetic error for the determination of 0.2-3 mg sodium is ca. 3%.

2. The use of mixtures of solutions of ammonia, ammonium carbonate, and o-hydroxyquinoline and ethyl alcohol for removal of contamination present in sodium and potassium salts permits determination of sodium not only in ash from plant material but in other natural objects as well.

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THE APPLICATION OF MATHEMATICAL STATISTICS IN ANALYTICAL CHEMISTRY[1)]

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Articles have started to appear recently in our analytical journals which have been devoted to the application of mathematical statistics in analytical chemistry, in which the advantages of this important branch of mathematics have been clearly demonstrated, and recommendations made for its application in evaluating control methods in technics. A number of actual questions in the practical application of mathematical statistics under the conditions of control work in factory laboratories has also been posed.

E.g., Gracheva [1] has put forward a formula for calculating errors and permissible errors in analytical results, and also a rule for excluding 'freak' errors from a series of results. This material is however not illustrated by actual examples.

The application of mathematical statistics is most fully treated in Komar's article [2], where the theoretical basis of this method is given, in addition to derivation and use of formulas together with actual examples of the use of the method in treating analytical results.

We are in full agreement with Komar's approach and the method he has recommended for laying out results.

Komar proposes, without adducing tables of results, to characterize the method by the following indices:

1) n – the number of analyses;

2) σ^2 and S^2 - the dispersion of an individual result and of the arithmetic mean;

3) $\epsilon_\alpha = t_\alpha \cdot S_x$ – the accuracy for a given confidence α;

4) the relation between dispersion and the initial concentration of the test material;

5) the relation between dispersion and the concentration of other materials.

It is however possible to detect systematic errors by a simpler method than that proposed by Komar. This is based on a comparison of the means of two series of analyses.

If there are no systematic errors, then it can be assumed that the means of two series of analyses are the approximate values of the same value E (mathematical expectation):

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1) Occasioned by N. P. Komar's article in J. Anal. Chem., 7, 325 (1952). [See Consultants Bureau Translation, page 361.]

if $\bar{x}_1 \approx E$ and $\bar{x}_2 \approx E$

($\bar{x}_1$ is the arithmetic mean of the first series of analyses, $\bar{x}_2$ the arithmetic mean of the second series of analyses), then $\bar{x}_1 \approx \bar{x}_2$.

The actual amount of material lies within the limits $E \pm \epsilon_\alpha$, where ϵ_α is the accuracy which is equal to $t_\alpha \cdot S_{\bar{x}}$.

A difference between $\bar{x}_1$ and $\bar{x}_2$ which is greater than ϵ_α indicates a displacement in the mathematical expectation, i.e., indicates the existence of a systematic error. Thus, if we consider Zolotukhin's results on the determination of beryllium as adduced in Komar's article, the presence of a systematic error can be established as follows:

If we accept as the true value one of 2.6550 mg/equivalent of beryllium which is the mean of a number of irreproachable results and then calculate the difference between this value and the value obtained by Zolotukhin's method, 2.6465 mg/equivalent, we get –

$$2.6550 - 2.6465 = 0.0085 = 8.5 \cdot 10^{-3} \text{ mg/equivalent.}$$

This difference is greater than the accuracy $\epsilon_\alpha = \pm 8.2 \cdot 10^{-3}$, thus indicating the existence of a systematic error. It is obvious that this method cannot be recommended for the analyses of large numbers of samples. Komar also treats the results of Golubtsova's method of determining niobium statistically; in this case for 11 replicates no systematic error could be found.

In some cases, systematic errors can be detected without recourse to calculation simply on the basis of the signs of the deviation of the results obtained from the true content. Since positive and negative values of random errors are of equal probability, then a sudden increase in the number of errors of the same sign points immediately to a systematic error. E.g., as in the determination of tin with the reagent 'anthrazo' proposed in 1945 by V. I. Kuznetsov.

One of the most important questions in analytical chemistry is the number of replicates necessary to give reliable results, since it is obvious that the most valuable method is the one which requires the least number of replicates to ensure a guaranteed accuracy.

This number can be calculated by means of a formula as shown in Komar's article. It is also possible to treat statistically two series of analytical results with different n.

V. A. Zolotavin recommends an in situ method for the determination of vanadium in ferrous alloys. In carrying out his determinations, Zolotavin made no less than six replicates from which he drew positive results. A statistical treatment of his tabulated results shows fewer determinations, e.g., four, would have been insufficient since the accuracy is not within the permitted limits. E.g., if we consider series b of the analytical results in Table 1 adduced by Zolotavin, this series contains results which are closest together, the accuracy (see table) is ±0.035%, i.e., outside the permitted limits of 0.025%. For six determinations (series b, Table 2), the accuracy, which is ±0.023%, is within the permitted limits.

On the basis of these results Zolotavin should have concluded that the irregularities in dissolving test material in the in situ method of determining vanadium by his method evened out when 6 analyses were made, and he should have recommended that this number of analyses should be carried out.

If the 'true' content of test element is known, then there is no need to use the cumbrous mathematical apparatus proposed by Komar for an arithmetical treatment of the results.

Statistical methods should be used when the "true" content of material is unknown, i.e., when there are no assay methods which can be used to give satisfactory results for comparison with the results obtained by the test method. E.g., arbitrary analytical characteristics of the type of the "oxidizability" of water, and the yield of volatile materials and coke in coal are assay methods of this type. They are useful for the study of redox potentials, for the study of the conditions under which reactions are best carried out when the mechanism is unknown, etc.

Tables of Results Obtained by V. L. Zolotavin
for the Determination of Vanadium by an in situ Method

(Vanadium content 0.58%)

Series b, Table 1

1	0.56
2	0.56
3	0.61
4	0.57
Mean	0.575

For 4 replicates:
$\Delta = 0.0175$
$\sigma_{\bar{x}} = 0.0220$
$S_{\bar{x}} = 0.0110$
$\epsilon_{\alpha} = 0.0350$

for a confidence of 0.950 and
$n = 4$; $\tau_{\alpha} = 3.18$

Series b, Table 2

1	0.62
2	0.53
3	0.59
4	0.58
5	0.58
6	0.58
Mean	0.580

For 6 replicates:
$\Delta = 0.0167$
$\sigma_{\bar{x}} = 0.0208$
$S_{\bar{x}} = 0.0085$
$\epsilon_{\alpha} = 0.0230$
for a confidence of 0.950 and
$n = 6$; $\tau_{\alpha} = 2.57$

Thus, the author of the present article calculated theoretical curves for the relation between the amounts of various oxidizing agents used for oxidizing organic materials in water. In particular, a comparison was made of the results of their oxidizability by permanganate and the "use of oxygen dissolved in the water." Complex curves were obtained which do not bring out the real relation. On the basis of these results, it was concluded that the existing methods of determination do not characterize the amount or the composition of the organic material in the water and require reexamination.

In studying methods of determining components, the "true" content of which can be established by other methods, there is no need to calculate graphical relations for establishing correlating formal relations between various factors. In these cases it is possible to determine experimentally a functional connection between the separate factors and the accuracy of analysis.

Mathematical statistics permits a correct evaluation of analytical methods and helps to plan future study and development. The application of statistical methods should be studied by analysts in all cases when practical necessity requires it. Mathematical statistics cannot replace experiment and is not an end in itself.

Received October 22, 1953.

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1)See Consultants Bureau Translation, page 51.
2)See Consultants Bureau Translation, page 361.

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DISCUSSION

From the Editorial Board

A Discussion Arising from an Article by M. B. Shchigol and N. B. Burchinskaya entitled "The Quantitative Determination of Trivalent Iron by Means of Tetraborate." [See J. Anal. Chem., 7, 289 (1952)][1], the critical observations made by A. K. Babko, Ibid., 8, 127 (1953)[2], and the answer of Shchigol and Burchinskaya to these criticisms, Ibid., 8, 185 (1953).[3]

The editorial board considers that A. K. Babko's criticism of M. B. Shchigol and N. B. Burchinskaya's article on the method employed by them for studying reactions between $FeCl_3$ and $Na_2B_4O_7$ in aqueous solutions and the conclusions drawn by them, is justified. The authors carried out a potentiometric titration of $FeCl_3$ with $Na_2B_4O_7$ in which they used platinum with platinum black as the electrode. In so far as the latter reacts sensitively to changes in hydrogen ion concentration which inevitably occur during titration, with borax, then the conclusions re complex formation with borate ions in the system considered cannot be regarded as clear cut and therefore, are inconclusive.

Shchigol and Burchinskaya explain the behavior of the electrode in their case, as an oxidation reduction process, on the basis that there is always a small amount of Fe^{2+} ions in solution of trivalent iron, and this small number of Fe^{2+} ions ensures a definite change in the oxidation-reduction potential of the system. This seems rather a far-fetched assumption. Moreover the Fe^{3+}/Fe^{2+} electrode may be sensitive to borate ions and may be no less sensitive to OH^- ions as well. We do not deny the possibility of complex formation in the system $Fe^{3+} - B_4O_7^{2-}$. We are only concerned with the deficiencies of the method employed to decide this question, since the method actually used leads to results which are possible of more than one interpretation. What has just been said is also applicable to the results of cryoscopic measurements of this system where the choice of the direction taken by the curve is somewhat arbitrarily chosen.

We may point out that the formation of complex silver cyanide in the system $AgNO_3 - KCN - H_2O$, where the alkaline media which is always formed in the second stage of the reaction (formation of $[Ag(CN)_2]^-$), would seem to give rise to a side reaction No one, however, has any doubts as to the direction taken by this reaction when one takes into account the relatively high solubility of AgOH on the one hand [which cannot be said about $Fe(OH)_3$], and the very high stability of the ion $[Ag(CN)_2]^-$ ($K_{instability} = 1.10^{-21}$), which, by the way, follows from the shape of the solubility curve of AgCN in KCN solutions (the slope is 45° despite the negligible solubility of AgCN, ca. 10^{-8} mol/liter), and finally, when one takes into account that a silver electrode which is sensitive to just these silver ions can be used in this system.

There is no need here to touch upon other less important aspects of the case under discussion, although perhaps we should refer to the basis of observations made by M. B. Shchigol and Burchinskaya in reference to an unfortunate expression of Babko's, viz., "it is well known that excess of a coordinating ions usually leads to the formation of a more stable complex." When the process of complex formation in a system is stepwise (just the case in point), this sentence of Babko's could be interpreted as meaning that each successive complex is more stable than the preceding one, which naturally Babko is not in a position to confirm. Here, however, we can only refer to the inaccuracy of the sentence; it would be more correct to say that excess of a

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1) See Consultants Bureau Translation, page 325.
2) See Consultants Bureau Translation, page 145.
3) See Consultants Bureau Translation, page 205.

coordinating ion does not form a more stable complex[1]), but only makes any of the complex compounds formed in the given system more stable.

Of greater importance is another fact, viz., the facility with which some authors draw far-reaching conclusions and recommend this or that value of a constant on the basis of rather unsuitable physico-chemical experiments. It is unfortunate that this reproachful practice, which is used for the formal interpretation of experimental results, is rather widespread; particularly when we are trained in our country in a school of chemical analysis according to the precepts of which systems which have complex chemistry should be studied by a number of methods in order to arrive at correct interpretations of the composition of compounds formed in the system on the basis of a study of property-composition diagrams, and in addition, of the composition of solutions not containing solid phases. First of all, it is essential to be sure of the correctness of our qualitative interpretation (composition of the compounds formed), and only when we are sure of this should we carefully consider the quantitative aspect of the case (calculations of constants, etc.).

The editorial board must agree with Shchigol and Burchinskaya that a study of the chemistry of borate compounds in solution is of great interest and deserves attention. The board is quite willing to place the J. Anal. Chem. at the disposal of anyone who wishes to publish work on this question, but with the reservation that from the methodological point of view, the work will be beyond reproach. Shchigol and Burchinskaya's first paper is an exception, though this does not mean that the editorial board shares the opinion of the authors with respect to some of their conclusions.

[1]) Incidentally, the word complex should not interfere with the substitution of the term, complex compound, or complex ion.

IVAN VLADIMIROVICH TANANAEV

(On His Fiftieth Birthday)

On the 4th of June 1954 Ivan Vladimirovich Tananaev, one of the foremost Soviet scientists, a Corresponding Member of the Academy of Sciences, a Stalin prize winner, a professor, and a doctor of chemical sciences, celebrated his fiftieth birthday and his thirtieth year of scientific and teaching activity.

His scientific and practical activity is unusually wide and varied. Tananaev, a talented pupil of N. S. Kurnakov, is well-known as an analytical chemist, an inorganic chemist, a skillful research worker, and a wonderful teacher.

Tananaev finished his course in the Chemical Faculty of the Kiev Polytechnic Institute in 1925 but stayed there in the Analytical Chemistry Department as an assistant and became a candidate for a higher degree. In 1928 he defended his thesis on "The action of oxalic acid on metal fluorides," which he completed under the direction of Prof. N. A. Tananaev, in whose laboratory he worked up to 1934. During this period he developed a number of new analytical methods for production control, including methods of determining potassium, zinc oxide, calcium oxide, calcium fluoride in fluorspar, fluorine in apatites and phosphorites, and tin, lead, antimony, and copper in Babbitt metal, etc.

In 1934 Tananaev moved to Tbilisi, where he worked as director of the Laboratory of the Chemical Institute of the Transcaucasian Branch of the Academy of Sciences. In a comparatively short time (1934-1935) he organized a large number of coworkers and carried out many important investigations. All this work, which can be regarded as the second stage of his scientific work, is characterized by the development of new analytical methods with a wide application of physico-chemical methods for the study of reactions.

Thus, Tananaev in conjunction with his coworkers, proposed tin amalgam for the rapid determination of Fe, Cu, Hg, Sn, Ti, Au, Pt, W, V and Ag; a potentiometric method for the determination of potassium using the ferrocyanides of Co, Ni, Mn and other metals; new adsorption and oxidation-reduction indicators: methyl violet, blue ethyl acid RRB, etc. New methods for the determination of Si, the alkaline metals, Mg, Ca, Al, and Fe as fluorides (fluorimetry) were also developed; and a systematic study was made of the solubility of precipitates and hydrolytic adsorption.

His activity in the Chemical Institute of the Georgia Academy of Sciences and in the Tbilisi Chemico-Technical Institute where he was the head of the chair of Analytical Chemistry, led to many fruitful results. It was during this period that the ground work was laid for the scientific researches which he is still developing at the present time.

His scientific activities reached their peak at the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences, where he went in 1935.

In 1939 he successfully defended his thesis for a doctor's degree taking as his subject, "The physico-chemical analysis of fluoride compounds and their application in analytical chemistry." He carried out this work under the direction of N. S. Kurnakov. While still working on his doctorate he studied at the laboratory of the Institute of General and Inorganic Chemistry in close contact with its director, Prof. B. G. Karpov, after whose death Tananaev became the

head of the laboratory. This laboratory was reorganized in 1948 into a laboratory of the Chemistry and Analysis of Rare Elements. Tananaev is still its director.

During this period Tananaev has been basically occupied with working on a number of problems related to the application of physico-chemical methods to analytical chemistry. In a series of investigations along these lines, Tananaev and coworkers in effect made a field, which had previously only been touched, a special field of analysis. Tananaev proposed a method based on the absorption of light by homogeneous and heterogeneous systems as a new method of physico-chemical analysis. He worked on a number of methodological questions connected with the study of the chemistry of interaction between ions in solution, and also on a number of theoretical questions and new criteria relating to the coefficient of molar extinction of suspensions and finding optimal conditions for turbidimetric analysis. This work was awarded the Kurnakov prize.

Tananaev was the first to adopt the method of measuring precipitate volumes as a physico-chemical method. The vast amount of material accumulated on this question is not only of great practical significance, but also opens up new perspectives for the study of the theory of formation and structure of analytical precipitates. In a series of papers published by Tananaev and coworkers entitled "Physico-Chemical Analysis of Systems of Analytical Importance," the principal results relating to the study of analytical reactions by the methods of light absorption, solubility, measurements of precipitate volume, E.M.F., etc. were laid out. This field has been developed widely in recent years in its application to the study of the chemistry of the rare elements according to a plan which did not have only an analytical slant, but was predominantly from a general and inorganic point of view. Compounds of the following elements were among those studied by Tananaev, et al: Rb, Cs, Be, Ga, In, Tl, Zr, Ge, Nb, Ta, Mo, W, and the rare earths. Tananaev paid particular attention to the fluorides and ferrocyanides of the rare elements. These investigations, which were carried out over a number of years, were distinguished by the care and accuracy with which the experimental part was carried out, accuracy being essential in dealing with such complex subjects. As a result of this work, a number of new compounds were prepared and studied for the first time; these included: $LiF \cdot HF$, $H_3AlF_6 \cdot 6H_2O$, $H_3AlF_6 \cdot 3H_2O$, $H_3FeF_6 \cdot 3H_2O$, $KTaF_6$, $KNbF_6$, $PbSO_4 \cdot 2K_2SO_4$, $K_4Ni_4[Fe(CN)_6]_3$, $5Cd_2[Fe(CN)_6] \cdot 4K_4Fe(CN)_6$, $11NaF \cdot 4FeF_3$, etc. Many of these found practical application. This work enriched the chemistry of salt-equilibrium and indicated new ways of preparing a number of salts on the commercial scale.

Of great importance is the work of Tananaev and his coworkers on the composition of cryolite; the old formula Na_3AlF_6 was shown to be incorrect, and a new formula $11NaF \cdot 4AlF_3$ was suggested. On the basis of this formula, Tananaev developed the "Cryolite" method of determining aluminum in the presence of Fe, Ti, Mo, W, V, Zr, and other elements. Work on the chemistry of fluorine led Tananaev in a similar way to develop a new method of volumetric analysis which he called fluorimetry.

In the course of his scientific work Tananaev and coworkers have carried out about 150 investigations. These investigations have raised the theoretical level and the importance of analytical chemistry in our country whereby a number of problems of contemporary chemistry has been solved, particularly problems connected with the chemistry of rare elements.

He has devoted a considerable amount of his time to teaching. He started teaching in 1925 and at various times has taught at the Kiev Chemico-Technical Institute, Tbilisi Chemico-Technical Institute, the Moscow Institute of Non-Ferrous Metals and Gold, and in the Minsk Polytechnic Institute. At present, he heads the Chemistry Section at the Moscow Engineering-Physical Institute. A characteristic feature of Tananaev is that he carries on research work at all the places he teaches, and attracts a large number of coworkers.

In parallel with his teaching and research work Tananaev directs the studies of pupils for various degrees. At present 23 of his students are candidates for degrees in various parts of the Soviet Union.

He has also played an important part in organizational and social work for many years being in charge of the Branch of the Chemistry of Rare Elements, a deputy director of the Institute of General and Inorganic Chemistry, and a member of the Bureau of the Div. Chem. Sci. USSR Academy of Sciences. From its inception he has been subeditor of the J. Anal. Chem., and editor of the Symposium on Chemistry of the Rare Elements.

He has been awarded the Order of the Red Star (1945), the Red Banner (1949) and the Order of Lenin (1954) for his scientific work. He has been awarded a Stalin prize twice.

This has been only a brief outline of his activities.

His contributions to analytical and general chemistry are considerable and are a new phase in the theory and practice of physico-chemical analysis.

He is at present in his prime.

On his birthday a wide circle of Soviet chemists, fellow workers, and scientists wish him the best of health and many further successes in his fruitful work for the good of our country.

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THE USE OF OSCILLOGRAPHIC POLAROGRAPHY FOR THE QUANTITATIVE DETERMINATION OF TITANIUM

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Many research workers have used a polarographic method for the determination of titanium in various objects. Zeltzer [1] got a reduction wave for titanium (IV) in weak acid media at a potential of −0.81 V (against the saturated calomel electrode). He reckoned that this wave corresponds to the process Ti (IV) + e ⟶ Ti (III). That this process was irreversible was shown by the fact that an anode oxidation curve of Ti (III) was obtained at a potential of −0.18 [2].

Acid solutions however are not very suitable for quantitative polarographic determination of titanium, since titanium salts are hydrolyzed in weak acid solutions, while in strong acid solutions (1-2 N) the titanium wave does not show up clearly and fuses into the H^+ discharge wave [2].

The use of complexing agents improves the shape of the wave, and methods have been worked out for the polarographic determination of titanium. The following materials have been used as complexing agents: tartrates, citrates [2], thiocyanates [3], oxalates [4], and Trilon B [5]. In these cases titanium (IV) forms a clearly defined wave with a half wave potential displaced to more positive values. Thus for the tartrate and citrate complex $E_{1/2} = -0.48$ V, while $E_{1/2}$ for the complex with Trilon B = −0.43 V (saturated calomel electrode) at a pH of 4.6. The titanium complexes are reversibly reduced, as one of us showed in the case of the complex with Trilon B [5]. The process can be schematically represented by the following reaction: Ti(IV) + e ⇌ Ti(III).

Zanko and coworkers developed a polarographic method for the determination of titanium in bauxite, kaolin, slags [6], casts, and steels [7], in which they used a 14% solution of tartaric acid in 0.1 N sulfuric acid as complexing agent. Using a calculating method they got relative errors of 4-5% for a titanium content of 0.4-1%. They did not study the effect of vanadium on the titanium wave.

Calculating methods [8] usually give errors considerably in excess of 4-5%, and the nature and concentration of other elements accompanying the titanium have a considerable effect on the value of the real diffusion coefficient of titanium.

1 N H_2SO_4 saturated with sodium oxalate and containing 8% urea as a maximum suppressor [4] was used for determination of titanium in clays. According to the author iron does not interfere, but the effect of vanadium was not studied.

A study of the value of $E^{1/2}$ for this complex showed that $E^{1/2}$ is independent of the concentrations of titanium and iron [9].

The preparation of a saturated solution of sodium oxalate in 1 N H_2SO_4 with a concentration of 8% urea is, however, impossible. In addition we could not establish that urea has a positive effect on the influence of iron on the titanium diffusion current.

Our aims were:

1. To develop a polarographic or oscillographic method of determining titanium in the presence of a number of elements: iron, vanadium, chromium, nickel, etc.

2. To elucidate the mechanism of the reduction of titanium (IV) complexes and to explain the stability of the tartrate, citrate, and oxalate complexes of Ti in 1-2 N sulfuric acid.

We accordingly studied the behavior of titanium (IV) complexes on the dropping mercury cathode in 1 N sulfuric acid using the ordinary and oscillographic polarographs.

EXPERIMENTAL

Apparatus. Measurements were made on a Heyrovsky photographic recording polarograph using a polarograph with a sensitivity of $2.21 \cdot 10^{-9}$ A/mm, and an oscillographic polarograph constructed by one of us. This instrument has been described previously [10].

The frequency of the saw-toothed vibrations of the generator was measured with a counter which registered the number of sweeps per unit time. The saw-toothed voltage applied to the cell was measured either with a tube voltmeter or potentiometrically. The cell consisting of a dropping mercury cathode and a saturated calomel electrode was well screened from interference. The drop time of the cathode (t) varied within the limits 6-7.3 seconds during oscillographic measurements, while the characteristics of the capillary used for polarographic determinations were as follows: $m^{2/3} t^{1/6} = 1.434$ $mg^{2/3} \cdot sec.^{-1/2}$ in 1 N solution of KCl – 0.05 N HCl at –0.8 V.

All the potentials quoted are referred to the saturated calomel electrode.

Solutions and Reagents. a) The stock solution of titanium sulfate was prepared by a three-fold treatment of an aliquot of potassium fluorotitanate with sulfuric acid, the mixture being heated to evolution of sulfuric fumes. The cooled solution was diluted to a known volume and the titanium content determined gravimetrically as TiO_2 after precipitation with ammonia. After dilution with 1 N H_2SO_4, 1 liter contained 0.2700 g Ti. b) Sodium oxalate, tartaric and citric acids were chemically pure or analytical grade chemicals; the hydrazine was recrystallized from water. c) Solutions of ammonium vanadate and of salts of Fe(III), Cr(III), Ni and Mo(VI) were prepared by the usual methods and their concentrations established chemically.

I. The Polarographic Wave of Titanium in the Presence of Iron and Vanadium

Titanium gives a clearly defined wave with $E_{1/2} = -0.3$ V in 1 N H_2SO_4 saturated with sodium oxalate. There is a straight line relation between the diffusion current and Ti concentration. The mean diffusion constant of the current is K = 2.0. In order to study the effect of iron and vanadium on the Ti(IV) diffusion current, various amounts of iron and vanadium (in 1 N H_2SO_4 saturated with sodium oxalate) were added to the test solution containing the same amount of titanium as in the solutions in which titanium was used on its own.

Fig. 1 shows that iron lowers the Ti(IV) wave by 40% for an iron concentration twice that of titanium.

When the Fe(III) concentration is four times that of titanium, the titanium polarographic wave is distorted and a maximum is formed on the polarogram (Curve 3, Fig. 1).

When the concentration of Ti(IV) and V(V) are roughly the same, the latter leads to an increase of 50% in the titanium wave as compared with the value of the Ti(IV) limiting current in the absence of vanadium. The origin of the titanium wave is not clearly shown (compare Curves 1 and 4, Fig. 1).

When the vanadium concentration is four times that of titanium, a maximum appears on the polarogram and the limiting current decreases with increasing applied potential, while the origin of the wave becomes indistinct as well (Curve 5, Fig. 1).

Ordinary polarography, therefore, cannot be used for quantitative determination of titanium in the presence of iron and vanadium without preliminary removal of the latter.

II. Oscillographic Curves of Titanium in Acid Media.

An oscillogram was taken of a $4.227 \cdot 10^{-4}$ M solution of Ti(IV) in 1 N H_2SO_4 (Fig. 2). The solution was electrolyzed at an amplitude of -1.4 V for the saw-toothed voltage in the absence of atmospheric oxygen. The oscillogram was recorded for one mercury drop at its maximum cross-section (at the point when the drop is falling off). Voltage applied to the polarographic cell is plotted along the abscissa while the current flowing through the cell is plotted along the ordinate. The oscillogram (Fig. 2) shows a curve rising sharply from the left, which is caused by the current from the charged mercury surface, the shape being determined by the impulse applied to the cell. The maximum value of the capacity current appears at an amplitude of $E \sim = -0.5$ V of the saw-toothed voltage. This is followed by a sharp fall in the curve to $E \sim = -0.77$ V. At a value of -0.81 V there is an increase in the current as the result of reduction of Ti(IV) ions. The maximum current I_{max} is -1.61 μA, at $E \sim = -1.4$ V, a discharge of hydrogen ions begins as a consequence of which the current increases rapidly.

Complexing agents (oxalic, tartaric, and citric acids) were added to the solution to improve the titanium oscillographic curve. In Fig. 3 an oscillogram is shown in which 1 N H_2SO_4 saturated with sodium oxalate and containing $4.277 \cdot 10^{-4}$ M titanium was used. This oscillogram also represents the process occurring on one mercury drop at maximum size. The surge at the beginning of the oscillographic curve corresponds to the capacity current. The maximum value of the capacity current is attained at a potential of -0.16 V, the current then remains practically constant up to a voltage of -0.3 V. At $E \sim = -0.3$ V the current increases rapidly as a result of the reduction of the Ti(IV) complex. The diffusion of Ti(IV) ions from the body of the solution to the layer near the electrode starts off from this point.

Starting from the reduction potential of quadrivalent titanium the current increases as a result of an increase in the concentration gradient in the layer adjacent to the electrode. The maximum value of current is reached at -0.5 V. After $E \sim = -0.5$ V there is a decrease in current strength; this is determined by a decrease in concentration gradient in the effective diffusion layer. Under the conditions which hold during oscillographic polarography, therefore, we get concentration polarization and I_{max} is a diffusion current for which $\left(\frac{\partial e}{\partial r}\right)_{r=0}$ has a maximum value. The value of the maximum titanium current for a $4.227 \cdot 10^{-4}$ M solution of titanium in 1 N H_2SO_4 saturated with sodium oxalate is 9.64 μA.

Figs. 2 and 3 were recorded for the same frequency of generator sweeps.

The oscillogram in Figs. 2 and 3 show that I_{max} of the Ti(IV) oxalate complex in 1 N H_2SO_4 is 6 times greater than I_{max} for hydrated Ti(IV) in 1 N H_2SO_4. The reduction potential of the Ti(IV) oxalate complex in 1 N H_2SO_4 is displaced by 0.51V to more positive values of E ~. This fact indicates that the Ti(IV) oxalate complex is stable in 1 N H_2SO_4. The Ti(IV) citrate and tartrate complexes, as our experiments showed, are destroyed at such low pH's; while E ~ of Ti(IV) in these media is −0.81 V and the value of the maximum titanium current is the same as in the absence of complexing agents.

It is possible to get clearly defined Ti(IV) waves in 1 N H_2SO_4 by the use of oscillographic polarography (Fig. 2), while this is impossible on an ordinary polarograph since the Ti wave fuses into the H^+ discharge wave (Fig. 4). In order to explain the reason for the large difference in the value of the maximum current of Ti(IV) in 1 N H_2SO_4 saturated with sodium oxalate and in the absence of oxalate, a number of measurements were made of the titanium diffusion coefficient in these media using diffraction methods. It was found that the diffusion coefficient of the Ti(IV) oxalate complex in 1 N H_2SO_4 is $7.22 \cdot 10^{-6}$ cm^2/sec, while D Ti(IV) in 1 N H_2SO_4 is $2.2 \cdot 10^{-6}$ cm^2/sec. Thus the diffusion coefficient of Ti(IV) in 1 N H_2SO_4 is approximately 3.3 times less than that of D for the Ti(IV) oxalate complex in 1 N H_2SO_4.

Titanium as the cation is known to be reduced in 1 N H_2SO_4. Since both the nature and concentration of an indifferent electrolyte affects the value of the cationic diffusion coefficient, then sulfuric acid as an electrolyte with 1,2 valencies significantly decreases the value of D of Ti(IV). The titanium diffusion current is accordingly small.

It is also known that [8] the value of the anionic diffusion coefficient increases on addition of an indifferent electrolyte, as in the case of the iodate ion. Probably sulfuric acid and excess $Na_2C_2O_4 \cdot 2H_2O$ has such an effect on the value of D for the Ti(IV) oxalate complex, increasing it to $7.22 \cdot 10^{-6}$ cm^2/sec.

As a consequence, the increase in the titanium diffusion coefficient in 1 N H_2SO_4 saturated with $Na_2C_2O_4 \cdot 2H_2O$, and the displacement of the reduction potential of the Ti(IV) complex to more positive potentials, indicate that at E ~ = −0.3 V it is the anion of quadrivalent titanium that is reduced. As a result the maximum current in 1 NH_2SO_4 saturated with sodium oxalate is greater than I_{max} for Ti(IV) in 1 N H_2SO_4 in the absence of sodium oxalate, for equal concentrations of titanium in both cases.

The time taken by the value of the Ti concentration gradient in 1 N H_2SO_4 saturated with $Na_2C_2O_4 \cdot 2H_2O$ to reach its maximum is 21 milliseconds.

In the case of the reduction of the quadrivalent titanium cation in H_2SO_4 of the same titanium concentration, but in the absence of a complexing agent the maximum value of $\left(\frac{\partial c}{\partial r}\right)_{r=0}$ of Ti(IV) is reached in 10 milliseconds.

III. The Effect of Rate of Potential Change on the Value of the Maximum Current of the Reduced Ti(IV) Oxalate Complex.

The effect of the rate of potential change on the value of the maximum current of the Ti(IV) oxalate complex in 1 N H_2SO_4 was studied.

The rate at which the potential applied to the cell changes (α) depends both on the frequency of the generator sweeps (ν) and on the amplitude of the saw-toothed voltage (E ~). The product of these two factors gives the rate of change of the saw-toothed voltage applied to the electrolytic cell. The following values were obtained for the maximum current (Table 1) for a $2.818 \cdot 10^{-4}$ M solution of Ti(IV) in 1 N H_2SO_4 saturated with sodium oxalate (in the absence of oxygen).

TABLE 1

Effect of the Rate of Change of Potential on the Value of the Maximum Reduction Current of Ti(IV). $2.818 \cdot 10^{-4}$ M Ti(IV) in 1 N H_2SO_4 saturated with $Na_2C_2O_4 \cdot 2H_2O$; m = 0.88 mg/sec; t = 7.1 sec, E ~ = 0.6 V (with respect to saturated calomel electrode); h = 440 mm; R = 1500 Ω

Frequency of the saw-tooth voltage generator, sweeps/sec (ν)	Rate of change of potential in V (α)	$\alpha^{1/2}$	Maximum current in μ A (found)
3.75	2.25	1.50	2.65
4.50	2.70	1.64	2.76
5.02	3.01	1.74	2.87
6.00	3.60	1.89	3.31
7.80	4.68	2.16	4.08
9.00	5.40	2.32	4.63
11.00	6.60	2.57	5.07
12.30	7.38	2.77	6.17
13.10	7.86	2.80	6.40
13.60	8.16	2.85	6.51
14.30	8.58	2.93	6.62

TABLE 2

Maximum Current Values for Various Ti(IV) Concentrations in 1 N H_2SO_4 Saturated with $Na_2C_2O_4 \cdot 2H_2O$; m = 0.88 mg/sec; t = 7.1 sec; ν = 12 sweeps/sec; α = 7.2 V/sec; h = 440 mm

μg Ti/ml	Concentration of Ti in mol/liter	Maximum current in μ A
27.00	$5.636 \cdot 10^{-4}$	11.91
20.25	$4.227 \cdot 10^{-4}$	8.93
13.50	$2.818 \cdot 10^{-4}$	5.95
6.75	$1.409 \cdot 10^{-4}$	2.98
2.70	$5.636 \cdot 10^{-5}$	1.20
1.35	$2.818 \cdot 10^{-5}$	0.60
0.67	$1.398 \cdot 10^{-5}$	0.30

The results given in Table 1 show that with increasing rate of change of the saw-tooth potential, the titanium maximum current increases. It is essential, therefore, when carrying out quantitative Ti determinations to work at a strictly constant rate of change of potential.

IV. Relation between the Titanium Maximum Current and Titanium Concentration.

Experiments were made in order to check the linear relation between the value of the maximum current of Ti(IV) and its concentration. To 1 N H_2SO_4 saturated with sodium oxalate was added various amounts of titanium, and the solution electrolyzed in the absence of atmospheric oxygen. Results are given in Table 2.

The results given in Table 2 indicate a linear relation between diffusion current and titanium concentration.

The sensitivity of the oscillographic method is considerably higher than that of the ordinary polarographic method. Curves 1 and 2, Fig. 5 correspond to a solution containing 1.0 and 0.4 μ g Ti/ml respectively in 1 N H_2SO_4 saturated with sodium oxalate. Curves 1 and 2 were taken for one mercury drop at its maximum size while Curve 3 was obtained on an ordinary polarograph in a solution containing 5 μ g Ti/ml in the same supporting electrolyte.

Despite the fact that the Ti concentration in Curve 2 is 12.5 times less than in Curve 3, the oscillogram is still clearly defined and can be used for quantitative determination of Ti. It is impossible to determine such a small amount on the ordinary polarograph. The high sensitivity of the oscillographic method as compared with the ordinary polarograph method is the result of the considerable difference in the rate of increase of the voltage in the impulse applied to the electrolytic cell.

V. Effect of Iron, Vanadium, Molybdenum, Chromium, and Nickel on the Value of the Maximum Ti Current

a) Effect of Iron and Vanadium.

Experiments in which solutions of vanadium and iron salts were added to the test titanium solution were made in order to establish the effect of iron and vanadium on I_{max} for Ti(IV) in 1 N H_2SO_4 saturated with sodium oxalate. The solutions were electrolyzed in the absence of atmospheric oxygen (Table 3).

TABLE 3

Effect of Various Concentrations of Iron and Vanadium on the Value of the Ti(IV) Maximum Current. m = 0.88 mg/sec; t = 7.1 sec; ν = 12 sweeps/sec; a = 7.2 V/sec; h = 440 mm

Expt. No.	Amount of metal taken in μg/ml			Maximum value of the Ti current in μA
	Ti(IV)	Fe(III)	V(V)	
1	10	–	–	4.41
2	10	25	–	4.41
3	10	50	–	4.41
4	10	100	–	4.38
5	10	250	–	4.39
6	10	1500	–	2.28
7	20	100	–	8.80
8	20	200	–	8.82
9	30	300	–	13.25
10	10	–	25	4.40
11	10	–	50	4.45
12	10	–	75	5.10
13	10	–	100	5.41
14	30	–	150	13.28
15	40	–	200	17.69
16	5	250	100	2.28
17	10	250	100	4.43
18	20	250	100	8.80
19	30	250	100	13.21
20	5	500	100	2.18
21	10	500	100	4.36
22	20	500	100	8.69
23	30	500	100	13.12

The results given in Table 3 show that trivalent iron does not affect the maximum diffusion current of Ti up to a ratio of iron to titanium of 25:1 (Experiments 1-5).

For higher ratios of Fe(III):Ti(IV) there is a decrease in the I_{max} of titanium (Experiment 6). Vanadium does not affect the maximum current of Ti until a ratio of V:Ti of 5:1 is reached, and the oscillographic wave of titanium begins to increase when the amount of vanadium in solution becomes 6 or more times that of the Ti(IV) concentration.

When both iron and vanadium are present simultaneously, their effect on the Ti current is not so pronounced as when they are present in the Ti solution separately. E.g., at a ratio of Fe:Ti of 100:1 and of V:Ti of 20:1, there is practically no effect on the value of I_{max} for titanium (Experiment 20, Table 3).

The linear relation between titanium concentration and the value of I_{max} within the titanium concentration range of 5-30 μg/ml is maintained even for a concentration of Fe(III) of 500 μg/ml and of V(V) of 100 μg/ml. Nevertheless for iron and vanadium contents which are respectively 100 and 20 times greater than the titanium concentration, these metals begin to affect the Ti(IV) oscillographic wave.

Fig. 6, e.g., represents the oscillograms obtained in 1 N H_2SO_4 saturated with sodium oxalate and containing various amounts of titanium, while the iron and vanadium concentrations are maintained constant.

Each curve represents the process which occurs on the mercury drop at its

maximum size. In all the test solutions Fe(III) = 500 μg/ml and V(V) = 75 μg/ml. Curves 1-4, Fig. 6 show that the titanium oscillographic curves are clearly defined and that the linear relation between the maximum current of Ti(IV) and Ti concentration is maintained with great accuracy despite the fact that the amounts of vanadium and iron are several times greater than that of titanium in the test solution.

A comparison of the oscillograms in Fig. 6 with the polarograms of Fig. 1 obtained with an ordinary polarograph shows that titanium can be determined in the presence of considerable amounts of iron and vanadium without a preliminary separation of the latter when an oscillographic method is used. This is impossible on an ordinary polarograph; in the latter case, Fe(III) and V(V) must be separated from titanium beforehand (Curves 1-4, Fig. 6, and Curves 2-4, Fig. 1).

b) Effect of Molybdenum, Chromium, and Nickel on I_{max} Ti.

Solutions of Ti(IV), molybdenum, chromium, and nickel in 1 N H_2SO_4 saturated with sodium oxalate were used for studying the effect of these elements on the maximum diffusion current of Ti. Results are given in Table 4. Solutions were electrolyzed in the absence of atmospheric oxygen.

The results given in Table 4 show that molybdenum has a considerable effect on the value of I_{max} for titanium. Even for a ratio of Mo(VI)/Ti(IV) = 0.6, the value of I_{max} for Ti(IV) increases by 15.7% (Experiments 1 and 2). For approximately equal amounts of Ti(IV) and Mo(VI) the latter increases the oscillographic wave of Ti(IV) by almost 30% (Experiment 3). The presence of iron and vanadium in a test solution containing Ti(IV) and molybdenum does not diminish the effect of Mo(VI) on the value of I_{max} for titanium. Chromium (III) and nickel (II) have practically no effect on I_{max} for titanium. In all cases the oscillographic wave of Ti(IV) is clearly expressed. Although molybdenum has this appreciable effect on the value of I_{max} for titanium, titanium can nevertheless be still determined in the presence of molybdenum if a calibration curve is taken for solutions containing Ti(IV) with the same amount of molybdenum in them as in the test sample.

TABLE 4

The Effect of Molybdenum, Chromium, and Nickel on the Oscillographic Wave of Titanium

m = 0.88 mg/sec; t = 7.1 sec; ν = 8.8 sweeps/sec; E ~ = −0.97 V; α = 8.53 V/sec; h = 440 mm

Expt. No.	Amount of metal taken in μg/ml						Maximum Ti(IV) current in μ A
	Ti(IV)	Mo(III)	Fe(III)	Cr(III)	V(V)	Ni(II)	
1	60.73	–	–	–	–	–	29.78
2	60.73	36.5	–	–	–	–	34.45
3	60.73	73.0	–	–	–	–	38.75
4	13.50	–	–	–	–	–	6.62
5	13.50	–	–	40.5	–	–	6.59
6	13.50	–	–	81.0	–	–	6.66
7	13.50	–	–	150	–	–	6.52
8	13.50	–	–	–	–	54	6.64
9	60.73	36.5	300	–	60	–	33.15

VI. An Oscillographic Method of Determining Titanium in Steels

Methods of determining titanium in steels containing vanadium, iron, cobalt, nickel, chromium, and copper usually take a long time and necessitate removal of some of these metals. The use of oscillographic polarography in this instance is therefore of interest.

A normal analysis takes 4-6 hours.

An oscillographic analysis takes 20 minutes after dissolving the sample. The following procedure was adopted:

0.5-2 g of steel turnings was dissolved in H_2SO_4, and HNO_3 added [11]. When the steel had dissolved, the acidity of the solution varied from 2-5 N with respect to H_2SO_4.

An amount of test solution was transferred to a 50 ml beaker such that the normality of the solution after dilution was exactly 1 N. The solution was then boiled with hydrazine sulfate to reduce any iron. When the solution had cooled, it was saturated with sodium oxalate and diluted to exactly 5 or 10 ml. The solution was then transferred to the electrolytic cell, hydrogen bubbled through to remove oxygen, and then electrolyzed. Having obtained the oscillogram, the value of the maximum current of titanium was determined, and the amount of titanium determined by the method of additions.

When the second oscillogram had been recorded, the initial concentration of Ti(IV) was calculated from the increase in diffusion current caused by the addition of a known amount of titanium. Determination of the maximum Ti(IV) current was done visually. Results for steel analyses are given in Table 5; results are also given for Ti content as determined by other methods in the Stalin Steel Institute.

TABLE 5

Determination of Titanium in Steels by Means of Various Methods

Sample No.	1	2	3	4	5
Composition of steel in %					
Carbon	0.58	1.05	1.02	0.15	0.14
Silicon	0.69	–	–	0.36	0.52
Sulfur	0.04	–	–	0.012	0.013
Phosphorus	0.026	–	–	0.022	0.031
Chromium	17.50	8.0	5.74	1.68	25.79
Nickel	8.58	–	0.13	0.21	0.31
Copper	0.24	–	0.06	–	0.34
Manganese	–	–	0.32	1.58	0.26
Aluminum	–	–	–	–	5.71
Cobalt	–	10.2	5.94	–	–
Vanadium	–	2.06	0.1	–	–
Results of determination of Ti in %					
Cupferron colorimetric method (Steel Institute)	0.40	–	0.69	0.037	0.031
Gravimetric method (Steel Institute)[1]	–	2.28	–	–	–
Oscillographic method	0.41	2.36	0.68	0.030	0.027
Difference in %	+2.5	+3.5	−1.45	−19.0	−13.0

1) Vanadium was separated from titanium by fusion with Na_2CO_3 and boiling with NaOH.

The results given in Table 5 show that those obtained by the oscillographic method are in good agreement with those of colorimetric and gravimetric determinations (with the exception of Samples 4 and 5). Since for the cupferron-colorimetric method of analyzing samples containing less than 0.05% titanium, a deviation between duplicates of ±20% was tolerated [11], then the agreement between the results of oscillographic and colorimetric methods for Samples 4 and 5 can be regarded as satisfactory. More accurate determinations

of titanium in steel can be made if the oscillograms are photographically recorded.

A number of oscillograms obtained for Ti(IV) in steels are adduced in Fig. 7 as examples.

Curve 1 corresponds to Sample No. 1, Curve 2 to Sample No. 3, while Curve 3 corresponds to Sample No. 3 after 0.5 ml of a standard solution of titanium has been added to the electrolytic cell. Oscillograms 1, 2, and 3 were recorded for one drop of mercury at its maximum size. Curve 4 corresponds to Sample No. 4 and was recorded during the growth of one mercury drop.

Oscillographic waves for titanium which appeared at a potential of −0.3 V are clearly defined and can be measured accurately.

The authors wish to thank Prof. A. M. Dymov for his gifts of steel samples.

SUMMARY

1. The reduction of titanium in acid media on a dropping mercury cathode has been studied by means of oscillographic polarography.

It has been established that titanium in the form of a cation is reduced in 1 N H_2SO_4 at −0.81 V (saturated calomel electrode). In a solution of sulfuric acid of the same concentration but saturated with sodium oxalate, it is the anion of the Ti(IV) oxalate that is reduced.

2. Investigation of the effect of tartrate and citrate on the titanium wave in 1 N H_2SO_4 showed that at this low pH both the tartrate and citrate complexes of Ti(IV) break down.

3. It has been shown that it is best to detemine titanium in acid media saturated with sodium oxalate.

4. It has been established that there is a linear relation between the titanium diffusion curve on the oscillograms and the titanium concentration of the solution.

5. The effect of iron, vanadium, chromium, nickel, and molybdenum on the maximum current of titanium has been studied. It has been shown that if the amount of iron is 100 and that of vanadium 20 times respectively, greater than the Ti(IV) concentration, then there is no effect on the value of I_{max} for titanium. Chromium and nickel also show no effect on I_{max} for titanium. Molybdenum, however, has a considerable effect on I_{max} for titanium and increases the current.

6. It has been established that normal polarography does not permit a quantitative determination of titanium in the presence of vanadium and iron without a preliminary separation of Ti(IV). The possibility has been demonstrated of determining titanium in steels without preliminary separation of vanadium and iron.

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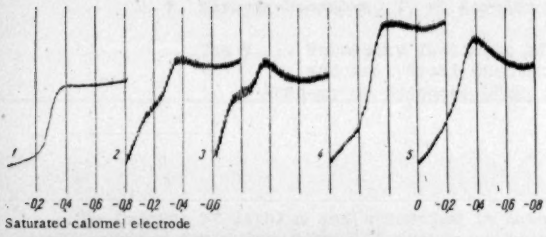

Fig. 1. Polarograms for titanium in presence of iron and vanadium.

Fig. 2. Oscillographic curve for titanium in 1 N H_2SO_4

Fig. 3. Oscillographic curve for titanium in 1 N H_2SO_4 saturated with sodium oxalate.

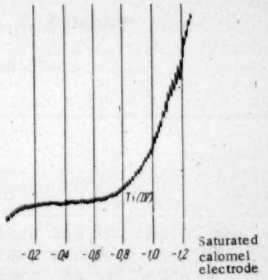

Fig. 4. Polarogram of titanium in 1 N H_2SO_4.

Fig. 5. Oscillographic curves of titanium (a) and a polarogram of Ti(IV) (b) in 1 N H_2SO_4 saturated with sodium oxalate.

Fig. 6. Oscillographic curves for titanium in the presence of iron and vanadium.

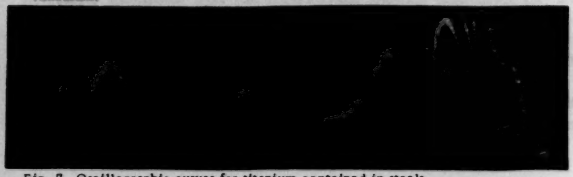

Fig. 7. Oscillographic curves for titanium contained in steels.

Spectroscopic Determination of Strontium and Lithium in Natural Waters – p. 295.

Fig. 1. Atomizer for spraying solution into the arc flame.

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SPECTROSCOPIC DETERMINATION OF STRONTIUM AND LITHIUM IN NATURAL WATERS

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The amounts of lithium and strontium in natural waters has interested research workers for a long time. A number of investigations has been devoted to the determination of lithium and strontium in sea water. On the basis of these results it has been accepted that the amount of lithium in sea water is $1.2 \cdot 10^{-5}$%; the amount of strontium is somewhat greater; according to a number of determinations including those carried out by A. P. Vinogradov and T. F. Borovik-Romanova, it is equal to $1 \cdot 10^{-3}$% [1]. There is considerably less strontium in river water; according to results obtained by one of the authors of the present article for a number of rivers in Western Trans-Baikal, it varies from $6 \cdot 10^{-6}$ to $7 \cdot 10^{-5}$%. The amount of lithium in river water according to V. I. Vernadsky's results ranges from $3.2 \cdot 10^{-6}$ to $1 \cdot 10^{-5}$% [2]. A. P. Vinogradov has pointed out more than once that for a better understanding of the origin of rocks and minerals and the method of migration of elements, a knowledge of the ratio between pairs of elements similar to each other in physico-chemical properties such as Ca/Sr, K/Rb, etc. is of considerable importance.

It has been found that the ratio of Ca/Sr is ca. 30 for sea water, while for river water, Ca/Sr is ca. 150 [3].

In the work described in this article determinations were made of strontium and lithium in a number of natural waters, mainly of chlorine, sodium and magnesium-containing waters (ca. 200 samples) of various origins. It was found that the amount of strontium in the waters tested varied from $1 \cdot 10^{-5}$ to $1 \cdot 10^{-3}$%, while the amount of lithium varied from $1 \cdot 10^{-7}$ to $1 \cdot 10^{-4}$%. The value of the ratio between calcium and strontium in the waters tested enabled us to assess whether the water was of sea or continental origin.

Method for the Determination of Strontium and Lithium in Natural Waters

In 1939-1940 S. A. Borovik and T. F. Borovik-Romanova worked out spectrographic methods for determining small amounts of strontium in solution by means of a condensed spark [4], and also by means of a D.C. arc. In the latter instance calcium was isolated from the test waters and its strontium content determined; lithium was determined by means of a flame. In 1950 S. A. Borovik and T. F. Borovik-Romanova used an H. F. spark for determinations of strontium in solution [5], and also an A.C. arc of the Sventitsky type in which a specially constructed atomizer was used [6]. By means of the condensed spark method it

was possible to determine $5 \cdot 10^{-4}$% Sr, but the sensitivity of the spark discharge method for lithium was low – $1 \cdot 10^{-3}$%; such sensitivity is not high enough for solving the problems we are interested in at present. The same is true of the H.P. spark. Since an activated A.C. arc of the Sventitsky type showed a sufficiently high sensitivity for determination of strontium and lithium, we chose this as an excitation source for simultaneous determinations of lithium and strontium in water.

We finally chose the following operating conditions: the excitation source was an A.C. arc operating at 120 V, with a current strength of ca. 2.0 A. The solution was sprayed into the arc flame by means of an atomizer (Fig. 1, see plate, page 293.) [5].

The atomizer consists of a quartz vessel 2 cm in diameter and 1 cm deep.

The vessel has a tubular nozzle, the top end of which is a ground glass cone. A carbon electrode 1.5 cm long is fitted into this cone, the upper end of the electrode is ground to a blunt wedge along which a narrow vertical groove is made, 3 mm deep, and in addition a channel 0.8 cm in diameter is drilled along the carbon axis. The channel terminates in side tubes on both sides of the carbon electrode near the bottom of the vessel; the channel serves to lift the liquid by capillary action to the upper end of the carbon electrode and ensures a continuous supply of solution to the arc flame.

The amount of liquid fed into the vessel is 1.5 cm^3.

A copper spiral is used as a current lead-in. The spiral, which at the same time is a spring, presses the contact, which is a copper wire with a platinum tip, to the lower end of the electrode.

The vessel is clamped in the arc stand.

The upper electrode is a carbon rod 6 mm in diameter, sharpened to a wedge, but without a groove.

The electrodes are mounted so that the edges of the wedges are arranged along the optical axis.

A three-prism glass spectrograph – the ISP-51 – with a camera of F = 270 mm, was used.

A two-lens system was used for illumination; the opening in the movable diaphragm was 3.2 mm, the arc length – 4 mm, the spectrograph slit – 0.02 mm[1], exposure time – 2 minutes. The arc was operated for 1 minute while the spectrograph slit was closed in order to get stable conditions for feeding the solution to the arc. The test waters were similar in composition to the dry residue, but differed in concentration, which

[1]) It is recommended that a two-stage clearing agent be fitted in front of the spectrograph slit.

was first adjusted by diluting or evaporating so that the dry residue in each case was ca. 0.015 g/cc. Standard solutions were prepared near in composition and concentration to the test solution; they contained 1.7% NaCl, 0.45% $MgCl_2 \cdot 6H_2O$, and 0.95% $CaCl_2 \cdot 6H_2O$, respective amounts of $SrCl_2$ and LiCl were added to these solutions. The final standards contained the amounts of strontium and lithium adduced in Table 1.

The solutions of the main elements contained insignificant amounts of strontium, the amount of strontium actually present was determined by the method of addition [7], and was taken into account with the amount of strontium added to the standard solution.

A solution of cesium nitrate containing 1% Cs was added in the ratio of 2:1 to the standard and test samples; cesium was used as the reference element.

For analysis the 4607.331 A line was used for strontium and the 6707.844 A line for lithium; the lines of the reference element were 4593.103 A and 6723.279 A.

The wave lengths and excitation potentials of the lines used are adduced in Table 2.

TABLE 1

No. of standard	Sr content, in %	Li content, in %
0	$8.1 \cdot 10^{-3}$	$6.6 \cdot 10^{-4}$
I	$2.7 \cdot 10^{-3}$	$2.2 \cdot 10^{-4}$
II	$9.0 \cdot 10^{-4}$	$7.3 \cdot 10^{-5}$
III	$3.0 \cdot 10^{-4}$	$2.4 \cdot 10^{-5}$
IV	$1.0 \cdot 10^{-4}$	$8.0 \cdot 10^{-6}$
V	$3.4 \cdot 10^{-5}$	$2.7 \cdot 10^{-6}$

TABLE 2

Wave length of test element (Å)	Excitation potential, in eV	Wave length of reference element (Å)	Excitation potential, in eV
Sr 4607.33	2.69	Cs 4593.103	2.70
Li 6707.844	1.80	Cs 6723.278	–

Panchromatic plates of sensitivity 1200 H. and D. were used for detection of lithium; the strontium line, however, was too intense when these plates were used. A device suggested by S. A. Borovik was accordingly adopted; the photographic plate was made in two parts: one ortho (or reproduction) and the other panchromatic. The panchromatic part was fixed in the part of the cell where the part of the spectrum from 5000-6730 A was incident, while the other part was located near the outer edge of the cell, where the 4250-5000 A part was incident. Samples and standards were photographed on the same plate, twice in each case. Using the ISP-51 spectrograph with an F = 270 mm camera, it was possible to get spectrograms of 23 samples and 4 standards on one plate. The blackenings of the lines indicated above for strontium, lithium and cesium were measured on a microphotometer in order to determine the strontium and lithium contents; the respective concentrations were determined from calibration curves plotted along the coordinates of ΔS, log C. Fig. 2 shows that the graph is linear for strontium within the limits $2.2 \cdot 10^{-4}$ to $6 \cdot 10^{-3}$, for lithium from $1.0 \cdot 10^{-5}$ to $5.0 \cdot 10^{-4}$%. The relative experimental error (mean arithmetic) was found for replicates to be $\pm$6-8%. Results of replicates for lithium are given in Table 3.

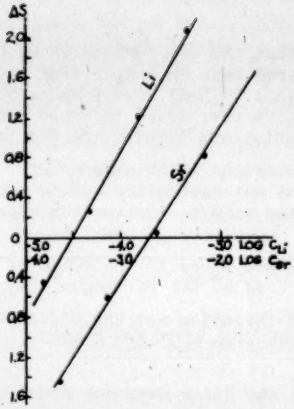

Fig. 2. Calibration curves for determination of Sr and Li in natural water.

TABLE 3[1])

Expt. No.	Amount of Li added, in %	Amount of Li found, in %	Relative error, in %
1	$2.7\cdot10^{-5}$	$2.7\cdot10^{-5}$	0
2	$2.7\cdot10^{-5}$	$2.6\cdot10^{-5}$	−3.7
3	$2.7\cdot10^{-5}$	$2.6\cdot10^{-5}$	−3.7
4	$2.7\cdot10^{-5}$	$2.9\cdot10^{-5}$	+7.4
5	$2.7\cdot10^{-5}$	$2.4\cdot10^{-5}$	−12.5
6	$2.7\cdot10^{-5}$	$2.8\cdot10^{-5}$	+3.7
7	$2.7\cdot10^{-5}$	$2.9\cdot10^{-5}$	+7.4
8	$2.7\cdot10^{-5}$	$2.6\cdot10^{-5}$	−3.7
9	$2.7\cdot10^{-5}$	$3.1\cdot10^{-5}$	+14.8

Table 4 contains the results obtained on one plate for the lithium and strontium content of some test waters. Each determination is the mean of duplicates.

These results show that the method worked out for determination of strontium and lithium in water is highly sensitive and is reasonably accurate.

TABLE 4

Sample No.	Concentration of Li in two parallel determinations, in %		Mean Li concentration, in %	Concentration of Sr in two parallel determinations, in %		Mean Sr concentration, in %
108	$1.26\cdot10^{-5}$	$1.22\cdot10^{-5}$	$1.24\cdot10^{-5}$	$6.6\cdot10^{-3}$	$5.0\cdot10^{-3}$	$5.8\cdot10^{-3}$
110	$0.9\cdot10^{-5}$	$0.7\cdot10^{-5}$	$0.8\cdot10^{-5}$	$7.5\cdot10^{-3}$	$8.0\cdot10^{-3}$	$7.8\cdot10^{-3}$
120	$0.8\cdot10^{-5}$	$0.7\cdot10^{-5}$	$0.75\cdot10^{-5}$	$9.8\cdot10^{-3}$	$9.8\cdot10^{-3}$	$9.8\cdot10^{-3}$
122	$4.2\cdot10^{-5}$	$4.9\cdot10^{-5}$	$4.6\cdot10^{-5}$	$4.0\cdot10^{-3}$	$4.0\cdot10^{-3}$	$4.0\cdot10^{-3}$
123	$1.6\cdot10^{-3}$	$1.9\cdot10^{-3}$	$1.7\cdot10^{-3}$	$14\cdot10^{-2}$	$16\cdot10^{-2}$	$15\cdot10^{-2}$
125	$7.4\cdot10^{-4}$	$7.0\cdot10^{-4}$	$7.2\cdot10^{-4}$	$4.2\cdot10^{-2}$	$3.6\cdot10^{-2}$	$3.9\ 10^{-2}$
126	$1.7\cdot10^{-4}$	$1.7\cdot10^{-4}$	$1.7\cdot10^{-4}$	$1.2\cdot10^{-2}$	$1.5\cdot10^{-2}$	$1.35\cdot10^{-2}$
145	$1.3\cdot10^{-4}$	$1.5\cdot10^{-4}$	$1.4\cdot10^{-4}$	$6.0\cdot10^{-3}$	$7.0\cdot10^{-3}$	$6.5\cdot10^{-3}$
150	$6.0\cdot10^{-5}$	$6.4\cdot10^{-5}$	$6.2\cdot10^{-5}$	$7.4\cdot10^{-3}$	$9.2\cdot10^{-3}$	$8.3\cdot10^{-3}$
158	$1.2\cdot10^{-5}$	$0.9\cdot10^{-5}$	$1.0\cdot10^{-5}$	$0.5\cdot10^{-3}$	$0.42\cdot10^{-3}$	$0.46\cdot10^{-3}$
171	$8.2\cdot10^{-4}$	$8.0\cdot10^{-4}$	$8.1\cdot10^{-4}$	$1.0\cdot10^{-2}$	$1.0\cdot10^{-2}$	$1.0\cdot10^{-2}$
182	$1.2\cdot10^{-4}$	$1.0\cdot10^{-4}$	$1.1\cdot10^{-4}$	$7.6\cdot10^{-3}$	$6.4\cdot10^{-3}$	$7.0\cdot10^{-3}$
187	$10.2\cdot10^{-5}$	$8.4\cdot10^{-5}$	$9.3\cdot10^{-5}$	$1.1\cdot10^{-2}$	$1.2\cdot10^{-2}$	$1.1\cdot10^{-2}$

We wish to express our thanks to A. P. Vinogradov and Prof. S. A. Borovik for their advice, and in addition we want to thank our coworker M. M. Farafanova who did some of the analysis.

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[1])Mean relative error = 6.3%. Sensitivity of determination by the method developed for Li = 3.10^{-6}%, for Sr = 1.10^{-5}%.

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DETERMINATION OF POTASSIUM WITH SODIUM TETRAPHENYLBORATE

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Sodium tetraphenylborate $Na[B(C_6H_5)_4]$ gives with potassium ions a white bulky, fine crystalline precipitate of $K[B(C_6H_5)_4]$, which is insoluble even in dilute (0.1 N) mineral acids. Potassium can therefore be determined by means of this reagent in acid media in the presence of a number of other cations and anions such as Li^+, Mg^{2+}, Ca^{3+}, Sr^{2+}, Ba^{2+}, Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, ClO_4^-, etc. The conversion factor (0.1091) to potassium from the borate is comparatively low, so that permissible errors are levelled down and even small amounts of potassium can be determined with great accuracy [1,2]. The fact that the reagent is not readily available, however, prevents its more widespread use in practice. Results are given in the present paper of gravimetric and volumetric determinations of potassium with sodium tetraphenylborate which was prepared by a simpler method which makes the reagent much more readily available.

Synthesis of Sodium Tetraphenylborate. To a solution of phenylmagnesium bromide prepared from 9.6 g magnesium and 60 g bromobenzene in 200 ml absolute ether cooled with water, is slowly added with vigorous stirring 8.8 g of the molecular compound of boron trifluoride and ether (b.p. 125-129°), dissolved in 30 ml absolute ether [3]. The reaction is carried out in a half-liter three-necked flask fitted with a reflux condenser, a dropping funnel, and a mechanical stirrer. It is best to use ground glass joints for the flask. An excess of phenylmagnesium bromide as shown by the appropriate color reaction [4] should be present. The reaction mixture is heated for 2 hours on a water bath. The ether is then removed under vacuum and the mixture heated on the water bath to boiling and the temperature maintained for 15-20 minutes at this temperature. The reaction mixture is cooled with water and 400-500 ml water added to it. If the temperature should rise, then the flask should be cooled again. A precipitate of magnesium fluoride separates out and a quantity of oily material comes to the surface. This solidifies when the reaction mixture is poured onto a flat dish. 45 g of sodium carbonate dissolved in a small volume of water cooled to room temperature is added to precipitate the magnesium. In order to facilitate filtration and to decolorize the solution, activated charcoal is added before filtration. The precipitate is difficult to wash so that it is best to strip it off the filter, mix it up with 400 ml of water and filter it again. Both filtrates are combined and saturated with sodium chloride. A white, bulky, precipitate of sodium tetraphenylborate settles out, which is filtered off, washed with saturated sodium chloride and dried in a vacuum desiccator over calcium chloride. The yield is ca. 30 g of raw material. This is extracted for 4-6 hours with absolute ether in a Soxhlet apparatus in order to remove impurities which interfere with potassium determinations. After extraction, ca. 26-28 g of material is obtained containing 45-50% of sodium tetraphenylborate, which corresponds to 55-60% of the theoretical, calculated on the boron trifluoride.

The reagent thus prepared is not completely pure and in addition to a

residue which is insoluble in water also contains water-soluble material. It should be made clear, however, that these materials do not interfere with the use of this reagent for gravimetric and volumetric determination of potassium.

The product is dissolved in water at room temperature. It is assumed that it contains ca. 50% sodium tetraphenylborate. A comparatively large residue thus remains undissolved and in order to coagulate this better, 1-2 ml of 0.1 M $Al(NO_3)_3$ is added, and the residue filtered (it is best to filter on the following day). The concentration of sodium tetraphenylborate in the solution thus obtained is determined by precipitation with excess potassium chloride under the identical conditions subsequently used for potassium precipitation.

A standard solution of chemically pure potassium chloride, the strength of which has been accurately determined, was used for standardizing the sodium tetraphenylborate reagent. In order to avoid errors connected with the use of burets, pipets, etc., 5-10 g of this solution was weighed out. The solution was acidified with acetic acid. The optimum pH of the solution should be 3-6 [1]. Some authors [5] prefer to precipitate in more acid solution, e.g., 0.1 N mineral acid solution. It has been found, however [1], that a decrease in pH leads to high results because of precipitation of decomposition products of the acid itself $[HB(C_6H_5)_4]$. Elevated temperatures lead to the same result. The test solution should therefore not be heated above 40°.

The following procedure can be recommended for the gravimetric determination of potassium.

Analytical Procedure. An aliquot of test sample 2-50 mg is transferred to a 100-150 ml beaker and diluted with an amount of water such that after precipitation from a solution containing 2 mg of potassium the final volume is ca. 10 ml, while for precipitation from a solution containing 50 mg, the volume is 70-100 ml. It is recommended that not more than 50 mg of potassium be used because of the bulkiness of the potassium tetraphenylborate formed. Acetic acid is then added in such an amount that at the end point its concentration in solution is 0.5-1%. The beaker plus test solution are heated on a water bath to 40°, when a 3.4% solution of sodium tetraphenylborate is added dropwise in 1.25-1.5 excess. The precipitate settles out comparatively quickly and after 10 minutes it can be filtered through a No. 4 glass or porcelain filter. The precipitate should not be left for more than 1-1.5 hours since long standing leads to high results, probably as the consequence of decomposition of $H[B(C_6H_5)_4]$. The solution is cooled to room temperature before filtration. The precipitate is transferred to the crucible by washing with small aliquots of liquid containing 1% acetic acid and 4 ml reagent/100 ml (10-30 ml of the wash solution is required); finally the precipitate is washed three times with small amounts of water, 1-3 ml. The precipitate is dried at 110-120° for 1/2-1 hour and then weighed. The potassium value is obtained by multiplying the weight of precipitate by 0.1091.

The results we obtained for potassium are given in Table 1. In experiments 9, 10, 11 , potassium was precipitated in the presence of ten times its amount of Mg, Ca, and Ba. These results can be regarded as completely satisfactory. In each case they are not inferior to those obtained by other workers using recrystallized reagents. This shows that the reagent as we prepared it is good enough for the determination of potassium, and that its recrystallization from methylal and chloroform is unnecessary. Moreover the recrystallized reagent is not completely soluble in water, as is evident from published results [1-5], a fact which we verified in our own case.

Volumetric Determination of Potassium

The volumetric method of determining potassium which we are putting forward is based on the precipitation of potassium by excess of a standard solution of sodium tetraphenylborate as in Rudorf and Zannier's method [6], but excess reagent

TABLE 1

Precipitation of Potassium with Sodium Tetraphenylborate

Expt. No.	KCl solution taken, in g	$K[B(C_6H_5)_4]$ precipitated in mg	K taken, in mg	K found, in mg	Error, in %	Notes
1	1.9765	65.9	7.16	7.19	+0.41	
2	1.9770	66.2	7.23	7.22	−0.13	
3	4.9614	169.7	18.65	18.61	−0.21	
4	4.9604	169.6	18.65	18.61	−0.21	
5	4.9912	192.7	20.98	21.02	+0.19	
6	4.9754	192.5	20.92	21.00	+0.38	
7	5.0027	192.3	21.03	20.98	−0.28	
8	9.9897	387.9	42.16	42.31	+0.35	
9	4.9859	194.5	21.10	21.22	+0.56	$MgSO_4$ added
10	4.9936	199.9	21.13	21.26	+0.62	$Ca(NO_3)_2$ added
11	4.9686	193.5	21.03	21.11	+0.33	$BaCl_2$ added

in our case is determined by titration with ammonium chloride and not with silver nitrate.

Test solution containing potassium as chloride, sulfate, or nitrate is acidified with 0.05 N HCl in such amount that after addition of the respective amount of ca. 0.05 N $Na[B(C_6H_5)_4]$ for precipitation of potassium, the solution has an acid reaction. Precipitation is carried out at room temperature and after 10 minutes the precipitate of potassium tetraphenylborate is filtered by suction through a filter crucible (sintered glass crucible No. 4). A solution of ammonium chloride is then added to the filtrate and the precipitate of ammonium tetraphenylborate thus formed also filtered off. Excess ammonium chloride is determined in the final filtrate by Krapivina's method [7,8]. Precipitation of excess sodium tetraphenylborate with ammonium chloride without preliminary filtration of the potassium precipitate, i.e., simultaneous filtration of potassium and ammonium tetraphenylborate, cannot be recommended, since when such a combined precipitate is allowed to stand the ammonium ions which are in solution start to replace the potassium ions in the precipitate, so that variable results are obtained when the excess ammonium is determined.

Analytical Procedure

Solutions required and their standardization:

1. 0.05 N HCl.
2. 0.05 N NaOH, free of carbonate.
3. Ca. 0.05 N solution of sodium tetraphenylborate prepared as described above by dissolving ca. 17.4 g $Na[B(C_6H_5)_4]$ in 1 liter of water. Before filtration, 5 ml of 0.1 M $Al(NO_3)_3$ is added to the solution to facilitate coagulation of the insoluble precipitate and increase the storage properties of the solution.
4. Ca. 0.03 N NH_4Cl prepared by dissolving 1.9 g NH_4Cl in 1 liter water. The NH_4Cl content is established by titration with 0.05 N NaOH by Krapivina's method [7,8].

To 20 ml of NH_4Cl solution is added a drop of methyl red and the solution neutralized with 0.05 N NaOH, 5 ml of 40% formaldehyde neutralized beforehand is then added, and the hydrochloric acid thereby liberated titrated with 0.05 N NaOH, using phenolphthalein as indicator. Methyl red does not interfere with this titration since it is decolorized before the phenolphthalein color appears.

The ratio of the concentration of NH_4Cl and $Na[B(C_6H_5)_4]$ must be determined also. To do this 15 ml of 0.05 N $Na[B(C_6H_5)_4]$ is added to 20 ml of 0.03 N NH_4Cl acidified with 2 ml of 0.05 N HCl. The precipitate of $NH_4[B(C_6H_5)_4]$ is filtered off (best by suction under vacuum) and washed 3 times with 5 ml of water. The filtrate is neutralized with 0.05 N NaOH, using methyl red as indicator; 5 ml of a neutral solution of 40% formaldehyde is then added, and the acid liberated titrated with 0.05 N NaOH; the excess NH_4Cl is thereby determined.

Determination of Potassium. To 5-10 ml of test solution containing ca. 20 mg potassium is added 2 ml of 0.05 N HCl and 15 ml of ca. 0.05 N $Na[B(C_6H_5)_4]$. The precipitate formed is filtered by suction after 10 minutes and then washed three times with 5 ml of water. 20 ml of ca. 0.03 N NH_4Cl is added to the filtrate, and the precipitate of $NH_4[B(C_6H_5)_4]$ which separates also filtered off after another 10 minutes and washed three times with 5 ml lots of water.

The filtrate is neutralized to the methyl red end point, 5 ml of formaldehyde solution is added, and the mixture titrated with 0.05 N NaOH to the red color of phenolphthalein. In order to calculate the potassium content it is necessary to know the standard titer of the NH_4Cl, which can be established if we have a knowledge of the potassium content of the test solution.

An Example of the Method of Calculation Employed. 13.6 ml of NaOH was used to titrate 20 ml of NH_4Cl. During titration of excess NH_4Cl on precipitation of 15 ml $Na[B(C_6H_5)_4]$ with 20 ml NH_4Cl, 2.85 ml of NaOH was used. From this it follows that 15 ml $Na[B(C_6H_5)_4]$ is equivalent to 13.6 ml − 2.85 ml = 10.75 ml NaOH or 15.81 ml NH_4Cl.

For titration of excess NH_4Cl in the case: test sample + 15 ml $Na[B(C_6H_5)_4]$ + 20 ml NH_4Cl, 12.7 ml of NaOH was used, which is equivalent to 18.63 ml of NH_4Cl. From this it follows that 20 ml − 18.68 ml = 1.32 ml of NH_4Cl has been used for the precipitation of excess $Na[B(C_6H_5)_4]$. For the precipitation of potassium during the analysis, $Na[B(C_6H_5)_4]$ equivalent to 15.81 − 1.32 ml = 14.49 ml NH_4Cl was used. Knowing that the aliquot of solution in this particular case contains 18.67 mg potassium, we can calculate that 1 ml of ca. 0.03 N solution of NH_4Cl corresponds to 18.67/14.49 mg potassium = 1.289 mg. NH_4Cl is thus standardized against chemically pure KCl. Knowing this titer, we can therefore in any case calculate the amount of potassium in the test sample from the number of ml of NH_4Cl used. The NH_4Cl titer should be checked every 2-3 days.

TABLE 2

Volumetric Determination of Potassium with Sodium Tetraphenylborate

Expt. No.	NH_4Cl, in ml	K found, in mg	K taken, in mg	Error, in mg	Error, in %
1	14.61	20.87	20.97	−0.10	0.48
2	14.67	20.96	20.94	+0.02	0.10
3	14.73	21.05	20.94	+0.11	0.52
4	14.73	21.05	20.94	+0.11	0.52
5	14.61	20.87	20.97	−0.10	0.48
6	14.49	20.77	20.84	−0.07	0.33
7	14.55	20.85	20.91	−0.06	0.29
8	14.67	21.03	21.05	−0.02	0.10
9	14.55	20.85	20.87	−0.02	0.10
10	14.61	20.94	20.94	0	0

Results are given in Table 2 for the titration of two series of solutions of chemically pure potassium chloride. The reagent solutions were prepared

separately for each series. These results show that our proposed volumetric method for determination of potassium gives satisfactory results and is not less accurate than the gravimetric method. Its main advantage as compared with the methods of Rudorf and Zannier is that it does not need silver nitrate.

SUMMARY

1. A simplified synthesis of sodium tetraphenylborate has been worked out.

2. It has been shown that the reagent as prepared by our method is suitable for gravimetric determination of potassium.

3. A new volumetric method of determining potassium is described.

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RAPID METHODS OF MICRO ELEMENTAL ANALYSIS

VIII. SIMULTANEOUS MICRO DETERMINATION OF CARBON, HYDROGEN AND PHOSPHORUS IN ORGANO-PHOSPHORUS COMPOUNDS CONTAINING C, H, O, P AND N

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INTRODUCTION

The chemistry of organo-phosphorus compounds has received even wider development in recent years. In addition to research on natural phosphorus-containing compounds and the necessity of controlling the phosphorus content of commerical samples, many scientific-research laboratories need rapid, reliable, and universally applicable analytical methods for phosphorus which do not require large amounts of test material.

The principles of determining phosphorus in organic compounds have been worked out for as long as 50 years. All the methods which are in use at present for the analysis of organo-phosphorus compounds can be divided into three stages: 1) mineralization, 2) quantitative separation of phosphorus in a particular chemical form, and 3) determination of the amount of this particular compound.

One very characteristic feature of organic phosphorus compounds becomes apparent immediately one tries to mineralize them – this is their stability. These compounds, particularly when C–P bonds are present in the molecule, exhibit a marked resistance to oxidizing agents and to temperature.

The most widely used method of mineralizing these compounds is mineralization with liquid oxidizing agents. The following mixtures are those most commonly used: $H_2SO_4 + K_2Cr_2O_7$; $KMnO_4 + HNO_3$; $H_2SO_4 + HNO_3$; and also K_2SO_4, $K_2S_2O_8$, $CuSO_4$, $Al_2(SO_4)_3$, Se. Although the oxidation conditions are very severe – high temperature, a long heating period (for tens of hours), and numerous repeat oxidations –, nevertheless one still comes across examples of incomplete mineralization [1].

Resort is often made to mineralization by fusion with certain alkaline reagents. These methods, however, quite often do not give quantitative breakdown of the test material [2]; during treatment in unsealed vessels loss of phosphorus is a possibility [3].

When the compound has eventually been successfully mineralized, the purely inorganic part of the analysis has to be carried out, viz., quantitative isolation of the ionic phosphorus (usually as the PO_4^{3-} ion) in a chemical form which is suitable for analytical purposes. Even if the method of determination chosen, e.g., a volumetric or colorimetric one, does not require actual isolation of the compound of interest, the final solution after mineralization contains such a variety of interferring ions in fairly large amounts that it is preferable to isolate the phosphorus-containing ion quantitatively from all the others. Hiterto the most specific precipitant for PO_4^{3-} ions has been ammonium molybdate,

which forms an insoluble complex $(NH_4)_3PO_4 \cdot 12MoO_3$. The latter is attractive to chemists because of its very advantageous conversion factor. The ratio of its molecular weight to the phosphorus it contains is 68:1. In micro-analysis it is possible to weigh a precipitate with such a composition on ordinary analytical balances [4]. The advantage given by the factor is, however, counteracted by the negative qualities of the complex; viz., changes in composition with precipitation conditions, composition of solution, treatment and drying of precipitate [5], the long and meticulous operations required during separation of the precipitate. In order to make the molecule even bigger, its capacity to combine with certain organic bases is also used; e.g., strychnine [6], hydroxyquinoline [7], quinine [8], antipyrine [9]. For rough determinations with accuracies of the order of $\pm 5\%$; centrifuging the precipitate and comparing its volume with that of a precipitate prepared in the same way from solutions containing known concentrations of PO_4^{3-} ions [10] is adequate.

The amount of ammonium phosphomolybdate is often determined gravimetrically, but it can also be titrated directly with alkalies, or excess of the latter may be determined after dissolving the phosphomolybdate precipitate in the alkali [11]. The amount of phosphorus in it can also be indirectly determined from its nitrogen content as determined by the Kjeldahl method [12] or from the amount of molybdenum determined polarographically [13]. When the precipitate is treated with a reducing agent ($SnCl_2$ + HCl, fresh $FeSO_4$, 1-amino-2-naphthol-4-sulfonic acid, hydrazine sulfate, hydroquinone, citric acid) [14], it is brought into solution as a colored complex: molybdenum blue, the amount of which is determined colorimetrically [15]. Methods have been worked out in which, on the one hand the specificity of ammonium molybdate is used, while on the other hand the difficulties connected with the separation of the phosphomolybdate precipitate are avoided. The precipitate is dissolved in ammonia and reprecipitated as $MgNH_4PO_4 \cdot 6H_2O$, which is calcined to magnesium pyrophosphate $Mg_2P_2O_7$ (when precipitation is carried out directly after mineralization, it is very difficult to achieve quantitative precipitation [16]). The colored complexes formed by the PO_4^{3-} ion with salts of vanadium [18] and cobalt [17] have also been used for colorimetric determination of phosphorus. Its concentration can be determined by amperometric determination with trivalent iron [19], and by titration with uranium salts [20] or cerium salts [21].

Physico-chemical methods of analysis usually find limited application because of insufficient accuracy. Most colorimetric methods can only be used for samples with low phosphorus contents or for trace determinations. In none of the methods indicated is the quantitative formation of phosphorus pentoxide in an atmosphere of oxygen used for the direct gravimetric determination of phosphorus in organo-phosphorus compounds. Moreover, no method has been developed for the simultaneous determination of other elements present as well as phosphorus.

Our problem was to develop a method based on new principles which would permit phosphorus to be determined rapidly and accurately, simultaneously with other elements; for this it was necessary to find more suitable conditions for the quantitative breakdown of organo-phosphorus molecules and to isolate phosphorus in a weighable form. This would lead on the one hand to reducing the time of a determination, and open up possibilities of simultaneous determination of other elements.

DEVELOPMENT OF THE METHOD

As a first step we tried to analyze compounds containing C, H, O, P and N. We tried a combustion method worked out in the Micro-Analytical Laboratory of the Institute of Organic Chemistry, Academy of Sciences, USSR [22] for the analysis of the test organo-phosphorus compounds. The test material was pyrolyzed in a small open quartz beaker placed in a quartz tube, the pyrolysis products being burned in a rapid stream of oxygen. Under these conditions the phos-

phorus of organo-phosphorus compounds is converted into phosphorus pentoxide [23]. Experiment showed, however, that it is difficult to determine phosphorus pentoxide as an ash remaining in the beaker, since, on the one hand, phosphorus pentoxide is extremely hygroscopic so that its weight varies, while on the other hand, because of its volatility it penetrates into the water and carbon dioxide absorption tubes, thereby upsetting the balance of all three elements — C, H and P. Apart from this, phosphorus pentoxide forms a thin coating around the carbon residue obtained as a result of pyrolysis, and this film prevents combustion of the carbon. Another undesirable feature of phosphorus pentoxide is its corrosive action on quartz.

In order to prevent volatilization of phosphorus pentoxide from the small quartz beaker and formation of a film around the carbon, we decided to use an internal absorbent; the aliquot of test material in a small beaker was accordingly strewn with a layer of a preparation with special properties. Thus such a preparation should be thermally stable under the combustion conditions employed, should react quantitatively with phosphorus pentoxide to form a stable compound, and at the same time should be indifferent to the other products of pyrolysis and combustion.

We tried out purified fibrous asbestos and granulated magnesium oxide. These materials have already justified their use fairly well for the analysis of such difficult-to-analyze materials as fluoro- and silico-organic compounds [24, 25]. We found, however, that the use of asbestos impregnated with vanadium pentoxide V_2O_5 [26] gave no better results than pure asbestos. Both asbestos and magnesium oxide can be used to determine phosphorus by their increase in weight as a result of phosphorus pentoxide take-up, but the results are not accurate enough. It is difficult to get both these materials to constant weight by calcining, they corrode the quartz tube, and because of their hygroscopicity [27], it is difficult to establish the correction to be applied in blank tests when they are strewn over the test material. When it is taken into account that only 1.0-1.5 mg of phosphorus pentoxide is formed from the normal amount of sample taken for analysis, the corrections to be applied vary from 100-200 μg, which mean a large error in phosphorus determinations. Nevertheless for the analysis of fluoro- and silico-organic compounds, in view of their special properties, more satisfactory absorbents than magnesium oxide and asbestos have not yet been found.

For analysis of organo-phosphorus compounds we tried to find materials which have a zero correction, i.e., materials which are non-hygroscopic. Pumice is a material which, while similar to asbestos in composition, differs from it in its physical structure; pumice has a large surface because of its porous character, but it is non-hygroscopic like fibrous powdered asbestos. When ground it is easy to transfer from one beaker to another; on calcining it rapidly attains a constant weight, and it does not corrode quartz.

Combustion of organo-phosphorus compounds in which pumice was used showed that the phosphorus pentoxide formed quantitatively during combustion is completely retained by the pumice placed in a small beaker; it is also possible to determine carbon and hydrogen simultaneously. We became convinced as the result of our tests that in order to achieve complete combustion of the test compound it is essential to have an excess of oxygen in the tube.

Preparation of Pumice

Pumice lumps are gradually milled down and a fraction with particle size of ca. 1 mm sieved off. The granules are treated with approximately 30% hydrochloric acid for 3-4 hours in round-bottomed flask on a boiling bath. They are then boiled a few times with water until there is no chloride left in the wash water. The air-dried pumice is calcined first in a muffle and then in a quartz tube at 900° in a stream of dry oxygen for ca. 8 hours. The material is kept in a flask fitted with a rubber stopper.

TABLE

Simultaneous Determination of Carbon, Hydrogen and Phosphorus

Expt. No.	Material	Weight taken, in mg	CO_2, in mg	H_2O, in mg	P_2O_5, in mg
1	$(C_6H_5)_3P$	4.815	14.555	2.470	1.280
	C-82.42; H-5.76; P-11.82	4.567	13.780	2.320	1.258
2	$(C_6H_5)_3CPO(OC_4H_9\text{-}i)_2$	3.399	9.193	2.268	0.568
	C-74.29; H-7.62; P-7.09	6.301	17.167	4.157	0.995
3	$(C_6H_5)_3CPO(OCH_3)_2$	5.493	14.366	2.835	1.101
	C-71.57; H-6.01; P-8.79	5.253	13.760	2.970	1.037
4	$C_6H_5NPC_2H_5(OC_2H_5)_2$	6.300	13.721	4.660	1.852
	C-59.73; H-8.36; P-12.84	5.490	11.932	4.130	1.622
5	$(C_6H_5)_3CPO(OC_3H_7\text{-}i)_2$	4.288	11.579	2.650	0.757
	C-73.51; H-7.16; P-7.58	5.702	15.314	3.390	0.991
6	$(CH_3)_2(CH_3CONH)CPO(OC_2H_5)_2$	7.470	12.501	5.687	2.240
	C-45.56; H-8.50; P-13.06	8.109	13.596	6.144	2.386
7	$CH_3COHNCH(C_6H_5)PO(OC_2H_5)_2$	5.112	10.224	3.306	1.263
	C-54.73; H-7.07; P-10.86	9.099	18.300	5.752	2.259
8	$(C_4H_9O)_2POCON(C_2H_5)_2$	3.951	7.749	3.427	0.971
	C-53.22; H-9.63; P-10.56	4.601	8.992	4.043	1.118
9	$(C_6H_5)NHCONHCH(C_6H_5)PO(OC_2H_5)_2$	7.455	16.256	4.239	1.457
	C-59.66; H-6.41; P-8.54	6.140	13.452	3.580	1.219
10	$(C_2H_5)_2NCOPO(C_2H_5)OC_4H_9$	4.947	9.592	4.350	1.389
	C-52.99; H-9.70; P-12.44	3.450	6.698	3.008	1.001

Analytical Procedure

Pumice thus prepared is loaded into the usual small quartz beaker used for combustion until its level after gentle tapping of the sides of the beaker is ca. 10 mm from the top; the beaker is wiped with shammy and passed through the oxidizing flame of a burner before placing it in a combustion tube of the set-up used for micro-determination of C and H; a second beaker is then placed in the combustion tube. The tube is sealed with corks and an electric oven moved on to the beaker + pumice, an absorption train for carbon dioxide, nitrogen oxides (if there is nitrogen in the test material) and water is then connected to the tube. 500 ml of oxygen is passed through the tube. The electric furnace is moved off, the absorption apparatus disconnected, wiped, and then transferred to the balance; the beakers are next removed from the tube, placed on a block and transferred to the balance also. The apparatus is weighed 15 and 20 minutes afterwards, and then connected up again to the combustion apparatus; about 6-8 mg of test material is placed in the empty quartz beaker (or a capillary containing the test material if it is liquid) and strewn with pumice from the other beaker. The total weight of beaker + aliquot of sample + pumice (taking into account the zero point of the balance) is taken at the 25th minute from the moment when the beaker containing the pumice was withdrawn from the combustion tube. Combustion is carried out in an oxygen stream, the throughput of which is 30-35 ml/minute.

When combustion is complete and when no more black zones of carbon are formed on the pumice on bringing the burner flame to the place where the sample

TABLE (continued)

Expt. No.	% C	Δ % C	% H	Δ % H	% P	Δ % P
1	82.49	+0.07	5.76	0	11.62	−0.20
	82.34	−0.08	5.67	−0.08	12.02	+0.20
2	74.33	+0.04	7.47	−0.15	7.29	+0.20
	74.35	+0.06	7.38	−0.24	6.89	−0.20
3	71.37	−0.20	5.76	−0.23	8.77	−0.02
	71.48	−0.09	6.33	+0.32	8.62	−0.17
4	59.43	−0.30	8.28	−0.08	12.83	−0.01
	59.51	+0.22	8.42	+0.06	12.89	−0.05
5	73.70	+0.19	6.92	−0.24	7.71	+0.13
	73.31	−0.20	6.65	−0.51	7.56	−0.02
6	45.67	+0.11	8.52	+0.02	13.09	+0.03
	45.75	+0.19	8.48	−0.02	12.84	−0.22
7	54.58	−0.15	7.24	+0.17	10.78	−0.08
	54.89	+0.16	7.07	0	10.84	−0.02
8	53.52	−0.30	9.71	+0.08	10.73	+0.17
	53.33	−0.11	9.83	+0.20	10.60	+0.04
9	59.51	−0.15	6.36	−0.04	8.53	−0.01
	59.79	+0.13	6.52	+0.11	8.67	+0.13
10	52.91	−0.08	9.84	+0.14	12.26	−0.18
	52.98	−0.01	9.76	+0.06	12.65	+0.21

is located, the end of the beaker is thoroughly heated, the burner is then moved away and the beaker allowed to cool for 5 minutes (with the oxygen still switched on). Next the electric oven is used to heat the tube for another 5 minutes. The operation is repeated. The oven is finally removed and the boat allowed to cool a little. The cork of the combustion tube is removed, and the oxidizing flame of the burner played up and down the length of the tube 2-3 times. The beaker is carefully removed, care being taken to see that no pumice falls out of it. The procedure is then the same as at the beginning of the analysis: the absorption apparatus is weighed at 15 and 20 minutes, and the boat at the 25th minute after removal of the beaker, etc., from the combustion tube. The increase in weight as a result of absorption of phosphorus pentoxide is calculated from the change in zero of the balance during the time of the experiment.

Calculation of Results

Carbon and hydrogen are calculated as usual, while phosphorus is calculated by means of the formula:

$$\% P = \frac{a.f}{S} \cdot 100$$

where a is the increase in weight as a result of phosphorus pentoxide absorption; this is taken as the difference between the weight of the boat after combustion and before combustion (after deducting the weight of sample taken); f is the conversion factor = $2P/P_2O_5$ = 0.4364; S = weight of aliquot.

DISCUSSION OF RESULTS

The method proposed represents a great saving of time because two of the steps mentioned in our opening remarks are combined into one, viz., mineralization, which occurs under exceptionally suitable conditions in our method, and the isolation of phosphorus in a particular chemical form; the third stage — determination of this chemical form — reduces to simple weighing of the beaker immediately after combustion. The combustion conditions employed permit carbon and hydrogen to be determined simultaneously with the normal accuracy for this type of analysis.

The efficiency of the pumice granules under the combustion conditions employed is the result of the cracking action of its large porous surface, and its abundance of sharp edges and corners [28, 29]. The phosphorus pentoxide formed reacts chemically with pumice in the immediate neighborhood where decomposition of the sample occurs. It is not a question of mechanical retention of phosphorus pentoxide fumes here, since phosphorus pentoxide can be normally removed by heating to ca. 300-400°. Pumice contains SiO_2, R_2O (alkaline), Al_2O_3 and iron oxides. All these components are capable of giving thermally stable compounds with phosphorus pentoxide, $SiO_2 \cdot P_2O_5$ is one of the characteristic compounds of phosphorus. A modification of this, silicyl metaphosphate (SiO^{2+}), which forms at the temperature which is developed during combustion (ca. 1000°), is extremely stable. The reaction is equimolar, so that calculations can be made on the basis of an increase in weight in the form P_2O_5.

Pyrolysis of the sample should be effected rapidly, as in the rapid combustion method of Korshun and Klimova [22]. When this is done, the carbon which is evolved is distributed over a large surface, i.e., a thin film is formed which can be burnt off rapidly. Accordingly there is no need to fear that the pyrolysis products will burn near the opening of the beaker. As experiment showed, combustion outside the absorptive layer does not lead to low results for phosphorus. Apparently the volatile pyrolysis products do not contain phosphorus; the latter is converted exclusively into phosphorus pentoxide, which reacts immediately with pumice, as can be observed from the change in color of the latter from rose to grey in the closed end of the beaker.

For most of the compounds we analyzed, it was sufficient to carry out two final heatings with the oven. In some cases, however, particularly for thermally stable compounds, such as the derivatives of triphenylmethylphosphinic acid (see Nos. 2, 3 and 5 in the Table), it was necessary to resort to gradual combustion by moving the burner to and fro several times near the sample. By doing this the sphere of reaction becomes rich in oxygen, thereby leading to complete combustion of the carbonized part of the sample.

Certain precautions must be taken during analysis. When sampling, particularly liquids, greases, and easily electrified solids, care must be taken to see that the liquids do not fall on the walls of the beaker used for combustion far from the bottom, otherwise low results may be obtained for phosphorus content. It must also be remembered that light lumps of pumice are easily electrified at low humidities and may therefore fly out of the container when being placed in, or removed from the combustion tube. The oxidizing flame of the burner is therefore used for discharging it as indicated above.

In analysis for phosphorus only, it is sufficient to have one container for oxygen and a purifying train of 2-3 tubes for combustion. In such cases a series of determinations can be carried out.

All weighings were made on a Russian-made balance — the VM-20, issued in 1953. Although this model is officially regarded as a semi-micro balance, micro analysis can be carried out with it when it is properly used.

At the moment we are successfully developing methods for the simultaneous

determination of C, H, P, and S in phosphorus-containing materials, using only one aliquot.

SUMMARY

A new method has been worked out for simultaneous micro determination of C, H, and P in compounds containing C, H, O, P, and N. One determination takes ca. 1.5 hours. Deviation from theory does not exceed 0.3%.

The advantages of this method are: its rapidity, the possibility of analyzing materials which are not decomposed by other methods, determination of carbon and hydrogen as well as phosphorus on one aliquot, and protection of the quartz apparatus from corrosion.

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ENERGY CHARACTERISTICS AND THE ANALYTICAL CLASSIFICATION OF IONS

K. B. Yatsimirsky

The fundamental energy characteristics of ions which determine their behavior in solution are – the electrostatic characteristic (the quotient, square of the radius divided by the ionic radius – z^2/r) and the electrical nature of the ion in aqueous solution (the covalent characteristic [1]). The first of these characteristics, viz. (z^2/r) determines the electrostatic interaction of a given ion with other ions or dipolar molecules, the second (K) is the tendency of an ion to form covalent bonds. Complete information on these characteristics is given in Table 1.

TABLE 1

Energy Characteristics of Cations

Ions	Ionic radius	$\frac{z^2}{r}$	Covalent characteristic in aqueous solution	Ions	Ionic radius	$\frac{z^2}{r}$	Covalent characteristic in aqueous solution
Singly charged cations							
Li^+	0.78	1.28	–1	Cu^{2+}	0.80	5.00	137
Na^+	0.98	1.02	18	Sn^{2+}	1.17	3.42	–
K^+	1.33	0.75	20	Pb^{2+}	1.32	3.03	156
Rb^+	1.49	0.67	23	Cr^{2+}	0.81	4.94	71
Cs^+	1.65	0.61	22	Mn^{2+}	0.91	4.40	85
Fr^+	1.78	0.56	–	Fe^{2+}	0.83	5.82	86
Cu^+	(0.98)	(1.02)	(30)	Ni^{2+}	0.78	5.12	97
Ag^+	1.13	0.88	57	Co^{2+}	0.82	4.88	93
Tl	1.49	0.67	59				
Doubly charged ions				Triply charged ions			
Be^{2+}	0.34	11.74	55	Al^{3+}	0.57	15.8	121
Mg^{2+}	0.78	5.12	57	Sc^{3+}	0.83	10.8	–
Ca^{2+}	1.06	3.78	34	Y^{3+}	1.06	9.43	54
Sr^{2+}	1.27	3.15	43	La^{3+}	1.22	7.37	37
Ba^{2+}	1.43	2.80	35	Ln^{3+}	0.99–1.18	9.1–7.62	39–54
Ra^{2+}	1.52	2.63	–	Ga^{3+}	0.62	14.5	219
Zn^{2+}	0.83	4.82	135	In^{3+}	0.92	9.80	226
Cd^{2+}	1.03	3.88	159	Tl^{3+}	1.05	8.56	290
Hg^{2+}	1.12	3.57	228	Cr^{3+}	0.64	14.06	151
				Fe^{3+}	0.67	13.42	197
				Bi^{3+}	1.17	7.70	290

On the basis of the values of these characteristics, it is possible to segregate the ions into clearly defined analytical groups. On this basis some new groups appear in addition to those known already. The introduction of these

new groups can be based not only on the respective energy relationships but also on the necessity of expanding further the existing classification so as to include all elements, including the rare elements.

The magnitude of the covalent characteristic (K) of ions in aqueous solution determines the behavior of ions to all reagents containing strongly polarized atoms, including some important reagents such as hydrogen sulfide and ammonium sulfide. All cations can be divided into three groups according to the value of (K).

1. Ions with a low (K), which form sulfides soluble in water or completely decomposed by water to give hydroxides.

2. Ions with average values of (K), which form sulfides insoluble in water but soluble in acids.

3. Ions with a high (K), forming sulfides which are insoluble in acids.

Let us consider the characteristics of these three groups in greater detail.

To the first group belong singly, doubly, and triply charged ions with (K) respectively less than 30, 70 and 190 kcal and also ions with four charges with a low (K):

$$Li^+\ Na^+\ K^+\ Rb^+\ Cs^+\ Fr^+$$
$$Be^{2+}\ Mg^{2+}\ Ca^{2+}\ Sr^{2+}\ Ba^{2+}\ Ra^{2+}\ (Eu^{2+})$$
$$Al^{3+}\ Sc^{3+}\ Y^{3+}\ La^{3+}\ Ln^{3+}\quad Ac^{3+}\ Cr^{3+}\ (V^{3+},\ Ti^{3+})^{1)}$$
$$Ti^{4+}\ Zr^{4+}\ Hf^{4+}\ Ce^{4+}\ Th^{4+}$$

According to general analytical classification these ions belong to the first two analytical groups of cations and to the first subgroup of the third analytical group.

A characteristic of this group of ions is that they have either a complete electronic structure of the inert gas type, or, where there is a high charge, a small number of 3d electrons (not more than 3).

The second group includes ions with two charges and with a (K) between 70 and 130 kcal, and ions with three charges with a (K) between 190 and 230 kcal:

$$Cr^{2+}\ Mn^{2+}\ Fe^{2+}\ Co^{2+}\ Ni^{2+}\ Zn^{2+}$$
$$Fe^{3+}\ Ga^{3+}\ In^{3+}$$

All these ions belong to the second subgroup of the third analytical group. The ions which belong to this group have an incomplete 3d shell, the number of electrons varying from 4 to 8. Doubly and triply charged ions with an 18 electron shell and a fairly high z^2/r (Zn^{2+}, Ga^{3+}, In^{3+}) belong to this group.

Ions with one, two, or three positive charges and a (K) exceeding 30, 130 and 230 kcal, respectively, belong to the third group. In addition to the usual cations of this group, there are also positively polarized atoms of the elements (cationoids), which do not form simple aquo-ions in aqueous solution, but form anions or complex ions. The oxidation state of the cationoids given below is denoted by Roman numerals:

$$Cu^+\ Ag^+\ Au^+\ Tl^+\ (Hg_2^{2+})$$
$$Cu^{2+}\ Cd^{2+}\ Hg^{2+}\ Sn^{2+}\ Pb^{2+}\ Pd^{II}\ Pt^{II}$$

---

1) Ln – the rare earth (lanthanide)

Au^{III} Tl^{3+} As^{III} Sb^{III} Bi^{3+} Ru^{III} Rh^{III} Ir^{III}
Ge^{IV} Sn^{IV} Mo^{IV} Re^{IV} Pt^{IV}
V^{V} As^{V} Sb^{V}
Mo^{VI} W^{VI}

Cations and cationoids which belong to this group have 18 or 18 + 2 electronic structures and structures with incomplete 4d and 5d shells. The exception is Cu^{2+}, which has an incomplete 3d group. Cationoids with an inert gas structure and in an oxidation state greater than 5, in the absence of strongly manifested oxidation properties (V^{V}, Mo^{VI}, W^{VI}), also belong to this group. When the oxidation properties are strongly expressed (Mn^{VII}, Cr^{VI}), the elements concerned do not form thio salts.

The ions enumerated above which have a high (K) belong to the fourth and fifth analytical groups according to normal classification.

The group of ions with mean values of (K) does not include many ions and need not be subdivided into smaller groups. The remaining two groups include a large number of ions and must therefore be subdivided. This subdivision can be carried out on the basis of the values of z^2/r for the ions.

The first group of ions can thus be divided into two subgroups:

1. Ions with values of z^2/r less than 6, which form hydroxides soluble in water or in ammoniacal buffers:

Li^+ Na^+ K^+ Rb^+ Cs^+ Fr^+ (NH_4^+)
Mg^{2+} Ca^{2+} Sr^{2+} Ba^{2+} Ra^{2+} (Eu^{2+})

Ions of the first two analytical groups belong to this subgroup.

2. Ions with values of z^2/r greater than 6 which form hydroxides insoluble in water and in an ammoniacal buffer:

Be^{2+} Al^{3+} Sc^{3+} Y^{3+} La^{3+} Ln^{3+} Ac^{3+} Cr^{3+} $(V^{3+}$, $Ti^{3+})$
Ti^{4+} Zr^{4+} Hf^{4+} Ce^{4+} Th^{4+}

These ions belong to the first subgroup of the third analytical group.

The numerous ions of the first subgroup (first and second analytical groups) can be divided into:

a) Doubly charged ions with an ionic radius greater than 1.05 Å.

Ca^{2+} Sr^{2+} Ba^{2+} Ra^{2+} (Eu^{2+})

These ions are precipitated by ammonium carbonate, oxalate, and sulfate in alcoholic solution. By a suitable choice of reagents it is possible to differentiate these ions further. Sulfate in aqueous solution precipitates cations with radii greater than 1.25 Å, chromate in acetate buffers precipitates ions with radii greater than 1.3 Å, etc. The lead ion has a radius of 1.32 Å and is therefore reminiscent of the ions enumerated under certain conditions.

b) Singly charged ions with a radius exceeding 1.3 Å.

K^+ NH_4^+ Rb^+ Cs^+ Fr^+

These ions are precipitated by very large anions $[PtCl_6^{2-}$, $Co(NO_2)_6^{3-}$, $HC_4H_4O_6^-$, $Bi(S_2O_3)_3^{3-}$, etc.]. As in the previous instance it is possible to differentiate these ions further. By using the anions: BiI_4^-, SbI_4^-, MnO_4^-, $SnCl_6^{2-}$, and others, it is possible to precipitate ions with radii greater than 1.49 Å (Rb^+, Cs^+, Fr^+).

In this way, on a basis of the study of the energy characteristics of ions,

we have brought out a new analytical group – the potassium group which has group reagents and possesses all the characteristic features of an analytical group. This group contains the same number of elements as the alkaline-earth metals, the cations included in the new group however are far less widely distributed. The Tl^+ ion (r = 1.49 Å) possesses some properties in common with the potassium group.

After separating the potassium group there still remain outside this group the ions of Li^+, Na^+ and Mg^{2+}, which do not have a group reagent. The Mg^{2+} ion has a fairly high $z^2/r = 5.12$, and in certain features approximates to the first subgroup of the third analytical group (low solubility of its hydroxide, slightly soluble phosphate, arsenate, silicate, etc.). In certain respects the Mg^{2+} ion approximates to the ions of the calcium group (low solubility of the carbonate), which is also explicable on the nearness of the z^2/r of Mg^{2+} and Ca^{2+}.

The number of cations and cationoids with a high (K) is also very large and can be divided into subgroups on the basis of the values of z^2/r. The cations and cationoids in this group can be divided into three main subgroups:

1. Ions with low values of z^2/r – less than 3.3 (singly charged and large doubly charged ions): Cu^+, Ag^+, Au^+, Tl^+, Hg_2^{2+}, Pb^{2+}, Pt^{II}.

These cations form slightly soluble chlorides and belong to the hydrochloric acid subgroup. The rather large doubly and triply charged ions Hg^{2+}, Pd^{II}, Bi^{3+}, which form slightly soluble iodides, border on this group.

2. Ions with average values for z^2/r: Cu^{2+}, Cd^{2+}, Hg^{2+}, Sn^{2+}, Pd^{II}, Bi^{3+}, Tl^{3+}.

3. Cationoids with high values of z^2/r and which form thio salts: Au^{III}, As^{III}, Sb^{III}, Ge^{IV}, Sn^{IV}, Pt^{IV}, Ir^{IV}, Re^{IV}, V^{V}, As^{V}, Sb^{V}, Mo^{VI}, W^{VI}.

In order to form stable thio salts, it is essential not only to have high values for z^2/r but high values of (K). For this reason the Hg^{2+} ion which has a very high value of (K) for a doubly charged ion, forms thio salts although it is not characterized by a high z^2/r. The classification is shown schematically in Table 2.

The charge, radius, and (K) of an ion are determined by its position in the Mendeleev periodic system. The distribution of ions in analytical groups is based on differences in their chemical properties, on differences in their energy characteristics, and, consequently in the final count is determined by their position in the periodic system.

A number of Soviet chemists have pointed out the essentially close connection between analytical classification of the ions and the periodic system. This has been developed in detail, particularly in Blok's work [2,3].

Blok showed that there is definitely a close link between the analytical classification of ions and the periodic law, and widely used a concept of the energy characteristics of the ion – "the total moment" (z/r). In our opinion Blok rather overemphasizes the significance of the electrostatic characteristic (z^2/r) of the ions and underestimates the significance of the covalent characteristic (K). (K) is only brought in indirectly when introducing empirical corrections for each series of ions with similar electronic structures. Blok does not take into account the different oxidation states of an element, but arbitrarily chooses only one of the oxidation states for each element. This choice is based on the fact that "ions which are present in aqueous solutions prepared for analysis are chosen" [3].

We cannot agree with such a proposition since if it is accepted that the consideration of groups of ions depends on the method of preparing material for analysis, then we should have to re-examine the question of the relation between the analytical characteristics of the ions and the periodic law in

TABLE 2

Classification of Cations on the Basis of Energy Characteristics

	Low covalent characteristic $K_I < 30$ $K_{II} < 70$ $K_{III} < 190$			
	Low electrostatic characteristic $z^2/r < 6$			High electrostatic characteristic $z^2/r > 6$
	Large singly charged ions $r \geq 1.3$ Å	Large doubly charged ions $r \geq 1.05$ Å	Stable ions	
Group reagents	Na_2PtCl_6 $Na_3[Co(NO_2)_6]$ $NaHC_4H_4O_6$	$(NH_4)_2CO_3$ $(NH_4)_2C_3O_4$ H_2SO_4 (alc.)	None	$(NH_4)_2S$ or NH_4OH
Ions	K^+ NH_4^+ Rb^+ Cs^+ Fr^+	Ca^{2+} Sr^{2+} Ba^{2+} Ra^{2+} (Eu^{2+})	Li^+ Na^+ Mg^{2+}	Be^{2+} Sc^{3+} Y^{3+} La^{3+} Ln^{3+} Ac^{3+} Cr^{3+} (Ti^{3+}, V^{3+}) Ti^{4+} Zr^{4+} Hf^{4+} Ce^{4+} Th^{4+}

	Mean covalent characteristic $70 < K_{II} < 130$ $190 < K_{III} < 230$	High covalent characteristic 30 135 230		
		Low values of $z^2/r < 3.3$	Mean values of $z^2/r > 3.3$	High values of z^2/r
Group reagents	$(NH_4)_2S$	H_2S in acid solution		
		HCl	–	$(NH_4)_2S$
Ions	Cr^{2+} Mn^{2+} Fe^{2+} Co^{2+} Ni^{2+} Zn^{2+} Fe^{3+} Ga^{3+} In^{3+}	Cu^+ Ag^+ Au^+ Tl^+ Pt^{II} Pb^{2+} Hg_2^{2+}	Cu^{2+} Cd^{2+} Hg^{2+} Sn^{2+} Pd^{II} Bi^{3+} Tl^{3+}	Au^{III} As^{III} Sb^{III} Ge^{IV} Sn^{IV} Pt^{IV} Ir^{IV} Re^{IV} V^{V} As^{V} Sb^{V} Mo^{VI} W^{VI}

accordance with changes in the method of preparation for analysis.

Klyachko and Shapiro [4] have pointed out the necessity of using such important characteristics of the element as the ionization potential and electrical nature and indicated in a general way methods of using these characteristics for establishing relations between an analytical classification of the elements and their position in the periodic system. Recently Klyachko proposed, also in a very general way, to use electronegativity as a single chemical energy characteristic. Such an approach has certain of the drawbacks considered already, as well as some definite advantages.

We have tried to indicate all the numerous states of oxidation. With this in view, when several different oxidation states, in the analytical sense, are present, the square enclosing the given element is divided into several parts; in the right hand side the properties of the highest oxidation states are indicated, while on the left hand side the properties of the lowest oxidation states are indicated. We have pointed out that ions formed by one and the same element in various oxidation states sometimes differ from each other more than

ions of two similar elements in the same oxidation state.

Typical elements which form anions distinguished by low values of the ionized atoms and highest oxidation states are concentrated at the top and right of Table 3. Elements of Groups V, VI, and VII in the highest oxidation states form typical anions (the vanadium, chromium, and manganese sub-groups) and also the analogs of iron in the eighth group.

There is a fairly clear division between elements with a low value of (K) which do not form practically insoluble sulfides, and elements with average and high values of (K). These are elements of Groups I, II, III, IV, and V which form inert gas structures or ones with a small number of 3d electrons. Only Cr^{3+} from Group VI belongs to this class. The value of (K) in sub-groups, as a rule, decreases from top to bottom; consequently neither molybdenum nor tungsten form ions precipitated by ammonium sulfide as hydroxides.

The division between the potassium and alkaline-earth groups is very clearly marked. Li^{+}, Na^{+} and Mg^{2+} remain outside the group, but it is possible to make quite a number of conclusions re their analytical properties from their position in the periodic system.

Mg^{2+} lies between Be^{2+} and Ca^{2+} but actually occupies an intermediate position between ions of the second and third analytical groups with respect to some properties (formation of practically insoluble hydroxides, basic carbonates, practically insoluble phosphates and other compounds). In the horizontal series magnesium is alongside sodium, and thanks to this fact has a number of reactions which justifies the allocation of this ion to the first analytical group.

Elements in the middle of the fourth period form ions characterized by mean values of (K). The exception is Cu^{2+}, which is distinguished by a very high (K). Here we have a manifestation of the tendency of (K) to increase with increasing number of d electrons, and for a sharp fall in (K) in an ion with an 18 electron shell.

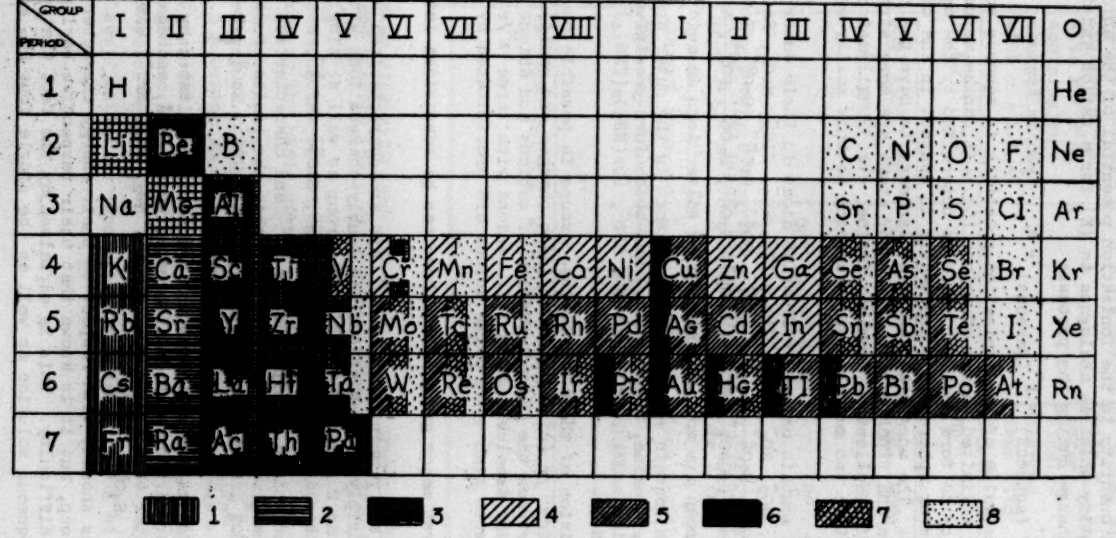
Ions with high (K) which form sulfides insoluble in acids are found mainly in the fifth and sixth periods. In this case we have a tendency for (K) to increase and the covalent character of the bond to strengthen in sub-groups of the Mendeleev system with increasing atomic number.

The formation of practically insoluble chlorides (and also of bromides and iodides) is characteristic of ions with a low charge, fairly large size, and high (K). As a result, ions of elements in the copper sub-group which are in a low state of oxidation, and ions in a low oxidation state but belonging to elements of the sixth period adjacent to the copper group, form insoluble chlorides. In all sub-groups, the sizes of the ions and their (K) increase with increasing atomic number; as a result the solubility of the halides in sub-groups decreases on moving from top to bottom.

Cations and cationoids with high (K) and Z^2/r respectively form thio-salts. The elements which form thio-salts are arranged in the form of three "islands." Certain elements of the sub-group of the V, VI and VII groups [V, Mo, W(Tl), Re] form one "island"— niobium and tantalum do not form thio-salts, apparently because their z_2/r is not high enough; chromium and manganese in the higher oxidation states are characterized by an exceptionally strong oxidizing action. The second "island" is formed by elements in the middle of the sixth period (Ir, Pt, Au, Hg), which are characterized by high (K). Elements mainly of the IV, V and VI groups (Ge, Sn, As, Sb, Se, Te) form the third "island". For the elements of these groups which belong to the sixth period, thio-salt formation is not characteristic, since in this case the higher oxidation states are extremely unstable (clearly expressed oxidizing properties), while ions of the elements in low oxidation states have a low z^2/r.

TABLE 3

Analytical Classification of Ions in D. I. Mendeleev's Periodic System



1) Singly charged cations precipitated by large anions; 2) doubly charged cation precipitated by sulfate; 3) elements which form practically insoluble hydroxides; 4) elements, which form sulfides insoluble in water, but soluble in acids; 4) elements which form sulfides insoluble in acids; 6) elements, which form practically insoluble chlorides; 7) elements which form thiosalts; 8) elements which form anions.

The behavior of anions in aqueous solution can be interpreted on the basis of the use of their z^2/r and (K) values in just the same way as the behavior of cations in aqueous solutions can be explained on the basis of the use of their energy characteristics.

The basic characteristic which determines the primary division of anions into groups is the magnitude characterizing the tendency of anions to form covalent bonds. Such a quantity is the ionization potential of the anion in aqueous solution – a quantity which is analogous to (K) for a cation and is determined by the energy change during the process:

$$X^-_{(aqueous)} = X^-_{(gaseous)} + e.$$

Unfortunately, the value of the ionization potential in aqueous solution can only be calculted for a limited number of anions [5]. It can be assumed, however, that the tendency to form covalent bonds is determined by the nature of the atom located in the outer sphere and consequently in contact in the crystal lattice with the cations. The ones with the least tendency to have their electrons distorted are hydrogen and fluorine anions. Other atoms are more strongly deformed (nitrogen, sulfur, chlorine, bromine, iodine, etc.). All anions can therefore be divided into two major groups according to this easily established characteristic.

1. Anions which contain oxygen or fluorine atoms in their outer sphere: F^-, HCO_2^-, $CH_3CO_2^-$, BO_2^-, NO_2^-, NO_3^-, BrO_3^-, ClO_3^-, IO_3^-, VO_3^-, ClO_4^-, MnO_4^-, ReO_4^-, BF_4^-, CO_3^{2-}, SiO_3^{2-}, HPO_3^{2-}, SO_3^{2-}, SeO_3^{2-}, TeO_3^{2-}, $C_2O_4^{2-}$, SO_4^{2-}, CrO_4^{2-}, SeO_4^{2-}, TeO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, MnO_4^{2-}, FeO_4^{2-}, RuO_4^{2-}, OsO_4^{2-}, SiF_6^{2-}, $S_2O_6^{2-}$, $S_4O_6^{2-}$, $S_2O_8^{2-}$, PO_4^{3-}, AsO_4^{3-}.

Anions of this group are not precipitated by silver ions in acid media.

2. Anions, which contain easily polarized atoms in the outer sphere (nitrogen, sulfur, chlorine, bromine, iodine, etc.) and which form precipitates in acid solution with silver ions: Cl^-, Br^-, I^-, CN^-, CNS^-, $[Cr(NH_3)_2(CNS)_4]^-$, S^{2-}, Se^{2-}, $S_2O_3^{2-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$.

A further subdivision of these anions into groups is possible on the basis of differences in their z^2/r (differences in ionic charges and radii). There is a definite relation between the characteristics of cations and anions during formation of practically insoluble salts [7]: anions with large z^2/r are precipitated by cations with high z^2/r, large anions are precipitated by large cations, etc.

Anions of the first major group noted above can be subdivided into three minor groups:

1. Anions which are precipitated by Mg^{2+} and are characterized by large values of z^2/r. All triply-charged anions and doubly-charged ions with thermochemical radii less than 2 Å belong to this sub-group as well as singly-charged ions with radii less than 1.4 Å: PO_4^{3-}, AsO_4^{3-}, CO_3^{2-}, SiO_3^{2-}, HPO_3^{2-}, F^-.

2. Doubly-charged anions precipitated by Ba^{2+} and characterized by average values of z^2/r. The radii of these anions lie within the limits of 2-3 Å: SO_3^{2-}, SeO_3^{2-}, TeO_3^{2-}, $C_2O_4^{2-}$, SO_4^{2-}, CrO_4^{2-}, SeO_4^{2-}, TeO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, MnO_4^{2-}, FeO_4^{2-}, RuO_4^{2-}, OsO_4^{2-}, SiF_6^{2-}.

3. Anions with low values of z^2/r which are not precipitated by Ba^{2+} and Mg^{2+} ions. Singly-charged ions with radii greater than 1.4 Å, and doubly-charged anions with radii greater than 3 Å: HCO_2^-, $CH_3CO_2^-$, NO_2^-, NO_3^-, BrO_3^-, ClO_3^-, ClO_4^-, MnO_4^-, ReO_4^-, BF_4^-, $S_2O_6^{2-}$, $S_4O_6^{2-}$, $S_2O_8^{2-}$.

BO_2^- and VO_3^- anions should, with respect to their energy characteristics also belong to this group, but it is known that their respective barium salts are only soluble with difficulty. This is explained by the fact that polymerized forms are present in aqueous solution as well as the single ions BO_2^- and VO_3^-.

TABLE 4

Classification of Anions on the Basis of Energy Characteristics

	Anions with fluorine or oxygen atoms in the outer sphere			
	High z^2/r (triply-charged anions, doubly-charged anions with $r < 2$ Å, and singly-charged anions with $r < 1.4$ Å)	Doubly-charged ions with 3 Å $> r >$ 2 Å	Low z^2/r (doubly-charged ions with $r > 3$ Å, singly-charged ions with $r > 1.4$ Å)	
			Large singly-charged ions with $r > 2.2$ Å	Stable ions
Cations of precipitant	Mg^{2+} Ba^{2+}	Ba^{2+}	Rb^+ Cs^+	None
Anions	PO_3^- AsO_4^{3-} CO_3^{2-} SiO_3^{2-} HPO_3^{2-} F^-	SO_3^{2-} SeO_3^{2-} TeO_3^{2-} $C_3O_4^{2-}$ SO_4^{2-} CrO_4^{2-} SeO_4^{2-} TeO_4^{2-} MoO_4^{2-} WO_4^{2-} MnO_4^{2-} FeO_4^{2-} RuO_4^{2-} OsO_4^{2-} SiF_6^{2-}	ClO_4^- MnO_4^- ReO_4^- BF_4^-	HCO_2^- $CH_3CO_2^-$ NO_2^- NO_3^- BrO_3^- ClO_3^-

	Anions with easily polarized atoms in the outer sphere	
	High z^2/r (quadruply-charged ions, triply-charged ions, and doubly-charged ions with $r < 2.3$ Å)	Low z^2/r (singly-charged anions and doubly-charged anions with $r > 2.3$ Å)
Cations of precipitant	Ag^+ in acid solution	
	Zn^{2+}	–
Anions	S^{2-} Se^{2-} $Fe(CN)_6^{3-}$ $Fe(CN)_6^{4-}$	Cl^- Br^- I^- CN^- CNS^- $[Cr(NH_3)_2(CNS)_4]^-$ $S_2O_3^{2-}$

Very large singly-charged anions which form precipitates with large singly-charged cations (Rb^+, Cs^+): ClO_4^-, MnO_4^-, ReO_4^-, BF_4^-, can be distinguished in this sub-group.

The anions of the second major group given above can also be divided into two sub-groups on the basis of the z^2/r values:

1. Anions with high values of z^2/r which are precipitated by zinc ions. Anions with three or four charges as well as anions with two charges and radii less than 2.3 Å belong to this group: S^{2-}, Se^{2-}, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$.

2. Anions with low values of z^2/r which are not precipitated by zinc ions (singly-charged and large doubly-charged anions): Cl^-, Br^-, I^-, CN^-, CNS^-, $[Cr(NH_3)_2(CNS)_4]^-$, $S_2O_3^{2-}$.

This classification is schematically shown in Table 4.

SUMMARY

1. An analytical classification of cations and cationoids on the basis of their energy characteristics is proposed. This classification corresponds to Menshutkin's classification in its most essential features.

2. The relation between the analytical classification proposed and Mendeleev's periodic system is demonstrated.

3. An analytical classification of anions on the basis of their energy characteristics is also proposed.

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A STUDY OF THE POSSIBILITY OF PREVENTING COPRECIPITATION OF COPPER WITH FERRIC HYDROXIDE

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Comparatively little study has been made of chemical methods of preventing coprecipitation in quantitative analysis. The interfering action of certain ions has been used in some cases. Thus, prevention of cation coprecipitation is achieved mainly by the use of ammonium salts and ammonium hydroxide, and also of acids [1]. Organic dyes which are good anion adsorbents may be used for counteracting anion coprecipitation. The issue is, however, not clear cut in all cases [2,3]. In some papers prevention of coprecipitation of contaminants is only touched upon indirectly [4]. In Ostroumov's papers [5], the use of chemical additives leads to a decrease in precipitate surface (formation of crystalline instead of amorphous precipitates), which results in practically complete prevention of adsorption of contaminants. It is possible that one of the reasons for this decrease in coprecipitation of strontium during precipitation of barium chromate in the presence of gelatin may also be a relative shrinking of precipitate surface [6]. Chepelevetsky [7] notes that in the case of coagulation of contaminants during (or after) crystallization, it is expedient to add protective colloids, which prevent contaminants from falling into the precipitate; in cases of adsorption and isomorphism it is possible to apply "masking," in particular, changing the interfering ion into an ion of different valency (e.g., reduction of Fe^{3+} to Fe^{2+}) or into complex ions, which are only sorbed to a very small extent by the precipitate (e.g., conversion of Fe^{3+} into a complex anion).

Our aim was to explain the effect of certain chemical additives on the amount of copper coprecipitated with hydrated ferric hydroxide when ammonium hydroxide is used for precipitating iron (III) from a solution containing iron (III) and copper (II). The work was done under unfavorable conditions, viz., a comparatively high concentration of iron and precipitation in the cold.

EXPERIMENTAL

Known volumes of solutions of $FeNH_4(SO_4)_2$ and $CuSO_4$ were introduced into centrifuge tubes, and certain additives introduced (except in blank tests) and, as a rule, the volume made up with water to approximately 33.5 ml. Iron was then precipitated with ammonium hydroxide in the cold. The precipitate was centrifuged and washed three times with hot NH_4Cl solution and, if necessary, a few more times with hot water. The washed precipitate of hydrated ferric hydroxide was then dissolved in 4 ml of ca. 2 N HNO_3, the iron was again precipitated with NH_4OH (1:1) and centrifuged. The volume of the centrifugate and the wash liquor obtained (the precipitate was washed three times with 5 ml of 2% NH_4NO_3) was made up to 25 ml in a standard flask. 10 ml of this solution was taken and after evaporation until no odor of ammonia was apparent, the copper was titrated amperometrically using the ferrocyanide method [8]. Since the amount of ammonium salts in the titrated solution varied (this was reflected to some extent in the titer of potassium ferrocyanide with copper), we titrated

the copper in the presence of a fairly large amount of ammonium nitrate. This ensured stable conditions and reproducible results. A needle galvanometer (1° = 10^{-8} A) was used for current measurement. The applied potential was 0.5 V. A saturated calomel half element with a large mercury surface was used as reference electrode. The anode was a polarized platinum micro electrode (d ≈ 1 mm, l ≈ 3 mm) rotating at 900 rpm. In addition to the test solution, the beaker used for holding the titrating solution also contained 20 ml of 1.5 M CH_3COONa, 0.5 g NH_4NO_3, and water to make up the volume to 40 ml. The whole was titrated against 0.025 M $K_4Fe(CN)_6$ (prepared daily); the latter was standardized against $Cu(NO_3)_2$ and was found to be equivalent to 1.899 mg Cu/ml.

We assumed that all the copper coprecipitated with the ferric hydroxide would appear in solution practically completely during the second precipitation. We also reckoned that the ferric alum in solution would affect the results of all experiments to an equal extent.

TABLE 1

Effect of Certain Additives on Coprecipitation of Copper

Expt. No.	Amount taken in mg		5 ml of saturated alcoholic soln. added	Total volume before pptn. in ml	Volume 0.0250 M $K_4Fe(CN)_6$ used in ml	Cu found in ppt. in mg	Copptd. Cu/Cu in %	Copptd. Cu/Fe in %
	Fe	Cu						
1	48.68	18.04	—	26	0.360	1.71	9.5	3.5
2	48.68	18.04	—	26	0.332	1.58	8.7	3.3
3	49.63	18.04	Safranine	31	0.320	1.52	8.4	3.1
4	48.68	18.04	Methyl blue	31	0.313	1.45	8.1	3.0
5	49.63	18.04	" "	31	0.284	1.34	7.5	2.7
6	49.63	18.04	Methyl violet	31	0.340	1.61	8.9	3.2
7	49.63	18.04	" "	10	0.203	0.96	5.3	1.9
8	49.63	18.04	Bismarck brown	31	0.277	1.32	7.3	2.7
9	49.63	18.04	" "	10	0.185	0.88	4.9	1.8
10	48.68	18.04	5% soln. of sodium salt of eosin	31	0.298	1.42	7.8	2.9
11	48.68	18.04	5% gelatin, 2 ml	31.5	0.248	1.18	6.5	2.4
12	48.68	18.04	1% agar-agar	31	0.320	1.52	8.4	3.1
			7.5 ml 4 N soln. added					
13	49.63	18.04	NH_4Cl	—	0.142	0.67	3.7	1.4
14	48.68	18.04	$N(CH_3)_3HCl$	—	0.208	0.99	5.5	2.0
15	49.63	18.04	Pyridine	—	0.259	1.23	6.8	2.5
16	49.63	18.04	Urea	—	0.381	1.81	10.0	3.6
17	49.63	18.04	Urotropine	—	0.353	1.68	9.3	3.4
18	49.63	18.04	"	—	0.150	2.80	15.8	5.7
19	49.63	18.04	NaCl	—	0.254	1.21	6.7	2.4
20	49.63	18.04	KCl	—	0.253	1.20	6.6	2.4

Note 1. In all the experiments the volume before precipitation was ca. 33.5 ml; the NH_4OH (1:1) was not added in excess (6 ml).

2. In experiments 3, 5, 7, 15, 16, 18, the solutions of additives were neutralized with HCl during preparation.

3. In experiment 18, 2.5 ml of the 25 ml was used for titration of the copper.

4. In the results given in this table and in all the remaining experiments, the copper coprecipitated, expressed as a percentage of the total amount of copper taken, is denoted as "Copptd. Cu/Cu in %", while when expressed as a percentage of the iron taken, it is denoted by "Copptd. Cu/Fe in %".

5. In experiments 7 and 9 the dye is destroyed by evaporation with H_2O_2 before titration of the copper.

6. In experiment 10 it is the cation Na^+ which has a retarding effect on the coprecipitation of copper, and not the eosin anion.

7. In experiments 10, 11, and 12, the additives are in aqueous solution, while in the last two, gelatin and agar-agar were added to try and cut down the surface of the $Fe(OH)_3$.

The results in Table 1 show that Bismarck brown was fairly successful in preventing coprecipitation of copper.

The use of dyes in analysis is, however, complicated by their limited solubility.

In practice the most satisfactory results are obtained by combining the action of ammonium salts with NH_4OH.

Table 2 contains results of experiments in which these were used. In particular we could not confirm the correctness of Stromberg, Dityatkovsky and Milovanova's assertions [9] that on precipitation of iron as hydroxide in the presence of Cu^{2+} ions (for definite ratios of these components) in solution with concentrations of NH_4Cl from 0.7-1 N, and of NH_4OH from 2.5-3 N, there is practically no copper adsorption (Table 2, experiment 9). Results are also given in this table of experiments carried out under the conditions recommended by N. A. Tananaev [10] (precipitation in concentrated solution), except that after precipitation it was cold water, and not hot water as the author suggested, that was used. A consideration of the results given in Table 2 shows that an

TABLE 2

Effect of NH_4Cl and NH_4OH on Coprecipitation of Copper

Expt. No.	Amount taken, in mg		Amount of 4 N NH_4Cl added, in ml	Volume of soln before pptn., in ml	NH_4OH added, in ml	Volume 0.0250 M $K_4Fe(CN)_6$ used, in ml	Cu found in ppt., in mg	Copptd Cu/Cu, in %	Copptd. Cu/Fe, in %
	Fe	Cu							
1	49.63	18.04	7.5	33.5	6 (1:1)	0.137	0.65	3.6	1.3
2	49.63	18.04	7.5	33.5	12 (1:1)	0.070	0.33	1.8	0.7
3	49.63	18.04	7.5	33.5	9 Conc.	0.056	0.27	1.5	0.5
4	49.63	18.04	7.5	33.5	18 "	0.026	0.12	0.7	0.3
5	49.63	18.04	7.5	33.5	20 "	0.045	0.21	1.2	0.4
6	49.63	18.04	7.5	12.55	20 "	0.034	0.16	0.9	0.3
7	49.63	18.04	0.00	4.55	20 "	0.037	0.18	1.0	0.4
8	49.63	18.04	7.5	12.60	20 "	0.033	0.16	0.9	0.3
9	49.63	9.02	7.5	33.5	18 (1:1)	0.035	0.17	1.9	0.3
10	49.63	9.02	0.00	33.5	18 (1:1)	0.076	0.36	4.0	0.7

increased concentration of NH_4OH in solution has a particularly favorable effect in decreasing the amount of Cu^{2+} adsorbed. In this connection it can be postulated that it is the complex-forming capacity of the latter which is chiefly responsible for the prevention of Cu^{2+} ion adsorption, and not the adsorption of ammonium ions and even of NH_4OH molecules (especially if we take into account Chepelevetsky's propositions [7]).

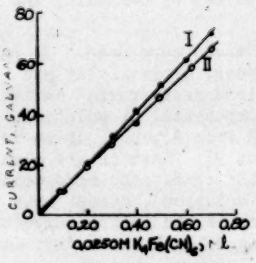
The use of glycine and ethylenediamine, which give even more stable complexes with copper than ammonia, gave good results (see Tables 3, 4 and dia-

gram). In the following series: ammonium hydroxide – glycine – ethylenediamine, the capacity to prevent copper coprecipitation increases with increasing stability of the respective copper complex; this is illustrated by a comparison of the instability constants of the latter [11]:

$$\frac{[Cu^{2+}]\cdot[NH_3]^4}{[Cu(NH_3)_4^{2+}]} = 2.1\cdot10^{-13}$$

$$\frac{[Cu^{2+}]\cdot[NH_2CH_2COO^-]^2}{[Cu(NH_2CH_2COO)_2]} = 5.3\cdot10^{-16}$$

$$\frac{[Cu^{2+}]\cdot[NH_2CH_2CH_2NH_2]^2}{[Cu(NH_2CH_2CH_2NH_2)_2^{2+}]} = 2.5\cdot10^{-20}$$



Titration curves for copper in 10 ml of the second centrifugate after precipitation of iron in the presence of: I – 0.5 g glycine; II – 100 mg ethylenediamine.

It should be noted that if the concentration of complexing agent used is too high, then iron also will form a complex which is not destroyed by ammonium hydroxide (e.g., for a concentration of 0.9 g glycine in 33.5 ml solution). Under the conditions given in Table 3, complex formation with iron is not observed, as proved by qualitative tests on the centrifugate obtained after precipitating 48.63 mg iron in the presence of 18.04 mg coppper in a volume of 33.5 ml. This test was carried out by evaporating small amounts of centrifugate with aqua-regia to destroy the glycine. No Fe^{3+} could be detected in the centrifugate thus treated.

It is also of interest to note that on adding glycine after precipitation of $Fe(OH)_3$ in the presence of Cu^{2+}, only small amounts of Cu^{2+} could be detected in the ferric hydroxide precipitate (Table 3, experiment 8). This confirms the adsorption character of coprecipitation of copper on ferric hydroxide and gives a picture of the mechanism of complex formation. Further work may lead to even better complexing agents.

These experiments showed that complex copper ions are adsorbed to a lesser extent than simple copper ions (or more accurately, aquo complexes). The explanation of this fact is to be sought in the fact that the radii of the first copper ions are bigger (the charge density is smaller) than the latter. It should also be remembered that the formation of inner complex compounds of copper decreases the charge on the complex to an even greater extent. In addition, the aquo complexes throw off the water "coat" comparatively easily, so that the copper ions are enabled to approach nearer to the adsorbing surfaces.

Karaoglanov [12] showed that on precipitation of H_2SO_4 with solutions of $Ba(NO_3)_2$, $BaCl_2$ and BaI_2, coprecipitation of barium decreased from nitrate to iodide. This can also be explained by complex formation, the tendency to which increases from NO_3^- – Cl^- – I^- from left to right. (Coprecipitation is decreased even more if BaI is added in the presence of NH_4I.) Our observation is confirmed by other similar examples adduced by Karaoglanov. It is also confirmed by other results ([1], p. 355).

TABLE 3

Effect of Glycine on Coprecipitation of Copper

Expt. No.	Amount taken, in mg		Glycine added in g	Amount of NH_4OH added in ml	Amount of 0.0250 M $K_4Fe(CN)_6$ used in ml	Cu found in ppt. in mg	Copptd. Cu/Cu in %	Copptd. Cu/Fe in %
	Fe	Cu						
1	49.63	18.04	0.3	6 (1:1)	0.065	0.31	1.7	0.6
2	49.63	18.04	0.4	6 (1:1)	0.033	0.16	0.9	0.3
3	49.63	18.04	0.5	6 (1:1)	0.010	0.05	0.3	0.1
4	49.63	18.04	0.5	6 (1:1)	0.000	0.00	0.0	0.0
5	49.63	18.04	0.5	6 (1:1)	0.011	0.05	0.3	0.1
6	49.63	22.55	0.5	6 (1:1)	0.029	0.14	0.6	0.3
7	49.63	27.06	0.5	6 (1:1)	0.039	0.19	0.7	0.4
8	49.63	18.04	0.4	6 (1:1)	0.015	0.07	0.4	0.1
9	49.63	18.04	0.4	9 Conc.	0.000	0.00	0.0	0.0
10	24.81	27.06	0.4	9 "	0.000	0.00	0.0	0.0

Note 1. In all cases the volume of solution before precipitation was ca. 33 ml. 2. In experiments 8, 9, 10, 1.6 g of NH_4Cl was added. 3. In experiment 8, glycine was added after precipitation of the iron.

TABLE 4

Effect of Ethylenediamine on Coprecipitation of Copper

Expt. No.	Amount taken, in mg		Ethylene-diamine added in mg	Amount of 0.0250 M $K_4Fe(CN)_6$ used, in ml	Cu found in ppt. in mg	Copptd. Cu/Cu in %	Copptd. Cu/Fe in %
	Fe	Cu					
1	49.63	18.04	50	0.008	0.04	0.2	0.1
2	49.63	18.04	50	0.013	0.06	0.3	0.1
3	49.63	18.04	100	0.000	0.00	0.0	0.0
4	49.63	18.04	100	0.000	0.00	0.0	0.0
5	49.63	18.04	100	0.000	0.00	0.0	0.0
6	49.63	18.04	100	0.000	0.00	0.0	0.0
7	49.63	22.55	100	0.000	0.00	0.0	0.0
8	49.63	27.06	150	0.000	0.00	0.0	0.0

Note. In all cases the volume of solution before precipitation was ca. 33.5 ml; NH_4OH (1:1) was not added in excess (6 ml).

The use of complexing agents during the precipitation of $Fe(OH)_3$ in the presence of copper does away with the necessity of a secondary precipitation, simplifies experimental technique, and opens up new possibilities in cases where excess NH_4OH cannot be used (e.g., during the precipitation of Al^{3+}).

In principle it follows that for any coprecipitating ion, it is possible to look for a specific complexing agent which does not act on the precipitated ion, while the interfering cations can be bound up into complex cations also, i.e., conversion of the first into complex anions is not compulsory [7].

Addition of the respective complexing agents, therefore, can be used as a general method for preventing adsorption, although there are grounds for thinking that these can also be useful in preventing such a form of coprecipitation as isomorphism [7].

SUMMARY

1. A study has been made of the effect of certain materials on the amount of copper coprecipitated during precipitation of hydrated ferric hydroxide with ammonium hydroxide from solutions containing Fe^{3+} and Cu^{2+}.

2. It has been established that the chief factor preventing coprecipitation of copper under the conditions used is complex formation.

3. It has been shown that in the series: ammonium hydroxide – glycine – ethylenediamine, the capacity for preventing coprecipitation of copper increases from left to right, i.e., with increasing stability of the respective copper complexes.

4. It has been established that at certain concentrations of glycine and ethylenediamine coprecipitation of copper during precipitation of hydrated ferric hydroxide by ammonium hydroxide in the cold is practically nil (for the concentrations of Fe^{3+} and Cu^{2+} used).

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1) See Consultants Bureau Translation, page 177.
2) See Consultants Bureau Translation, page 303.

REMARKS ON A METHOD BASED ON FRACTIONAL CRYSTALLIZATION OF THE DOUBLE NITRATES OF MAGNESIUM AND THE RARE-EARTH ELEMENTS

G. Virts

One of the methods which has been recommended for a long time for the separation of mixtures of the rare earths of the cerium groups is fractional crystallization of the double magnesium nitrates of these elements. Crystallization of solutions of these salts is usually carried out by cooling hot solutions in the air without stirring, whereby a coarse crystalline film is formed. Sometimes, though rarely, stirring during cooling is recommended; in such cases a fine crystalline mass instead of a compact mass is formed [1].

Quantitative results which would permit a comparison of the efficiency of the different techniques of crystallization to be made are not available in the literature.

The results set forth in this paper, however, show that these purely methodological factors have considerable significance in deciding the efficiency of separation by fractional crystallization.

Appreciable differences in the efficiency of fractionation were observed when mixtures of cerium earths were subjected to fractional crystallization of the double magnesium nitrates, according to the method of crystallization employed. This observation was the reason we decided to carry out some experiments to find out the most favorable method of crystallization.

A mixture of cerium earths was used for these tests, of the metals contained, cerium was removed practically completely, while most of the lanthanum was separated and some of the praseodymium. The composition of this mixture was as follows: La 5%, Ce < 0.1%, Pr 6.5%, Sm 4.5%, Ga 3%, yttrium earths ca. 2%, the remainder Nd. A solution of the double magnesium nitrate salts of the components in this mixture was prepared in the usual way.

When this method of crystallizing the double magnesium nitrate salts is used, it is possible to divide the rare earths indicated above into two groups: the less soluble one containing the elements neodymium, praseodymium, and lanthanum (the group called the "didymium group" and denoted by the symbol Di) and the more soluble one, containing samarium and the elements which follow it (here called the "smarium group" and denoted by the symbol Sa). The large difference in the solubility of the double magnesium nitrate salts between neodymium and samarium is characteristic.

Radioactive europium was added to the nitrate solution for quantitative control of crystallization. Europium is a typical element of the samarium group and is suitable for tracing the distribution of this group among the various fractions.

After separation of the mother liquor from the crystalline mass, the rare earths contents of both fractions were determined. Further by counting the β-impulses on a Geiger-Muller counter, the content of radioactive europium was determined in aliquots of the oxides of both fractions. For denoting the result of fractionation, the coefficient of fractionation K was calculated by means of the formula:

$$K = \frac{\text{Amount of Di-oxides}}{\text{Amount of Sa-oxides}} \quad \text{(in the crystals)} \qquad K = \frac{\text{Amount of Sa-oxides}}{\text{Amount of Di-oxides}} \quad \text{(in the mother liquor)}$$

For the determination of K according to the results available, i.e., from the rare earths content in the crystalline mass and the mother liquor used from the number of impulses/minute/mg of the oxides of both fractions, it was assumed on the basis of the composition given above that the amount of added radioactive europium represents ca. 10% of those rare earths in the original material which were designated as the samarium group. Although the assumption is not quite unarbitrary, nevertheless the errors to which it can give rise do not lead to appreciable distortions of the results given below.

In the first experiments (see Series A, Table 1), the original solution was evaporated and the hot solution cooled slowly in the air so that crystallization was spontaneous. It was found that spontaneous crystallization only proceeds in a regular manner for strongly supersaturated solutions. The values of K obtained thus are relatively low and vary considerably.

TABLE 1

Relationship between Fractionation Efficiency and Method of Crystallization

Expt. No.	Series	% Crystallization	Impulses/min/mg of oxide		K	Notes		
			In crystals	In mother liquor				
1	A	48.3	3.42	15.86	5.3			
3	A	67.3	5.45	18.16	3.9			
4	A	58.0	4.28	16.08	4.3			
5	A	63.7	6.18	16.79	3.1			
6	B	59.6	2.97	19.60	9.3			
8	B	61.8	3.93	19.85	6.1			
9	B	71.3	4.97	22.30	5.5			
						Cooling conditions °C		
						From	To	Minutes
10	C	61.1	2.45	21.20	10.7	74	25	31
13	C	64.2	2.95	21.95	12.7	89.5	23	55
11	C	64.2	1.35	23.75	15.6	88	22	95
12	C	63.6	2.06	21.90	13.6	91.5	25	300

Original material: 9.56 impulses/minute/mg oxide.

On an average, better, though still variable fractionation results were obtained by seeding the hot solutions, followed by slow cooling in air (see Series B, Table 1). Here, in contrast to the experiments of Series A, crystallization starts from the hot solution, but even in these cases supersaturation could be observed.

In the third series of experiments (see Series C, Table 1), a method which is rarely used in practice was adopted. The hot solution was seeded and then stirred vigorously with a mechanical stirrer, and then fairly rapidly cooled to room temperature with continued vigorous stirring. Small but well-formed crystals developed when this technique was employed. They were separated from

the mother liquor by squeezing them well and long on a Nutsch filter. When this method was adopted and the conditions were maintained constant the reproducibility was reasonably good. Crystallization rate has a marked effect on fractionation efficiency. Experiments, the results of which are given in the table, differ from each other in cooling rate.

Very rapid cooling gives poor fractionation probably because equilibrium cannot be fully established between the surface of the growing crystal and the solution. Under the conditions employed, however, even a one-and-a-half hour period of recrystallization gave maximum fractionation efficiency. Results of the fractionation obtained under the conditions of the 11th experiment can be regarded as very favorable.

The influence of the other factors was also studied while using the conditions of Series C. Thus it is interesting to know what values of K are obtained for varying degrees of recrystallization of the rare earths. In the experiments of Table 1, Series C, 61-64% of the rare earths was recrystallized. Some subsequent experiments with the same starting material were carried out under the same conditions as those employed in experiment No. 11. In these experiments, despite vigorous stirring there was initially some supersaturation; it became appreciable in the course of a few minutes for a relatively more complete crystallization, while the temperature of the solution increased by one or more degrees. The temperatures reached during this increase are indicated in the third column of Table 2. Determination of this temperature is a comparatively sensitive method of determining the extent of crystallization from the hot solution. The boiling point of the neutral salt solutions can also be used for this same purpose.

TABLE 2

Relationship between the Fractionation Coefficient and the Extent of Recrystallization of Rare Earths

Expt. No.	% Recrystallization	Temperature of crystallization °C	Impulses/min/mg oxide		K
			Crystals	Mother liquor	
17	43.3	57.3	1.40_3	15.0_0	12.5
14	51.2	66.5	1.46_0	16.8_2	13.9
19	64.5	75.7	1.91_3	21.7_0	14.5
18	65.4	78.1	1.89_5	22.1_5	15.1
15	74.1	86.0	3.09	25.9_2	11.4

Original material: 9.56 impulses/min/mg of oxide.

Experiment showed a small (hardly exceeding the experimental error) increase in the fractionation coefficient on increasing the amount of crystallized material; for an even greater degree of crystallization a fall in the fractionation coefficient occurs. In these experiments, of course, one cannot expect a constant value for K. A constant value can only be expected under isothermal crystallization conditions and when a thermodynamic equilibrium between the crystals and mother liquor exists. Moreover one of the components should be present in micro amounts [2].

If crystallization is carried further there should be an appreciable error, as a result of incomplete separation of crystals from mother liquor. This leads to a decrease in K. In addition, stirring the crystals and mother liquor towards the end of crystallization (at least as far as the conditions used in our experiments were concerned) becomes mechanically difficult. If it is desired to crystallize out more than two-thirds of the rare earths from a neutral solution, then particular attention must be paid to stirring during crystallization and to as full a separation as possible after crystallization.

The significance of the fractionation efficiency for fractions of different composition is of some interest for the application of this crystallization method. Table 3 contains results of some experiments carried out on fractions poor in the Sa group; i.e., fractions obtained from the crystals. It is possible to assess the composition of these fractions from the number of impulses/minute/mg of oxide, which is approximately proportional to the content of the Sa group of elements in the respective fraction. At the bottom of Table 3 are shown results for fractions rich in the Sa group. These experiments were also carried out under the conditions used in experiment No. 11 (Table 1). In calculating K the changing composition of the original solution with respect to the Sa group is taken into account.

TABLE 3

Relationship between the Fractionation Coefficient and the Content of the Samarium Group in the Original Solution

Expt. No.	Impulses/min/mg of original solution	% Crystallization	Impulses/min/mg		K
			Crystals	Mother liquor	
25	0.39_4	66.3	0.063	1.27_2	20.4
22	1.92	65.2	0.365	5.62	16.1
20	1.92	70.2	0.417	5.77	14.6
18	9.56	65.4	1.89_5	22.1_5	15.1
21	22.5	50.0	6.11	36.9	9.6
24	22.5	57.7	7.35	43.7	10.0
28	43.7	25.1	18.57	51.0_5	4.8

Results are somewhat better for fractions which are poor in Sa group elements, while the results are worse in cases where the fractions are richer in the Sa group. With regard to the latter it should be noted that the neutral solutions of the double magnesium nitrate salts rich in Sa crystallize out the poorer, the more the contaminants of the original material, such as iron, calcium and alkaline elements concentrate in the fractions rich in Sa.

These results show that fractional crystallization of the double magnesium nitrates is a suitable crystallization method for getting fractions rich in samarium and gadolinium from mixtures of cerite earths (ca. 10%) poor in these elements. A one-stage crystallization of two-thirds of the material is sufficient to decrease the content of the Sa group in a rare-earths mixture by five times.

Experiments described here with mixtures of cerite earths can be applied without any difficulty to rare-earth mixtures which are richer in lanthanum or containing cerium (III), since the double magnesium nitrates of these elements are slightly more sparingly soluble than those of neodymium.

SUMMARY

The effect of crystallization method on the efficiency of fractionation of mixtures of cerite earths, using fractional crystallization of double magnesium nitrates, has been investigated. Using radioactive europium, the separation of cerite earths into a less soluble fraction (Nd, Pr, La) and a more soluble fraction (Sm and the rare earths which follow it) was carried out almost quantitatively.

These methods of crystallization were: 1) spontaneous crystallization with slow cooling of the hot solution in air without stirring; 2) seeding the hot solution followed by slow cooling in air without stirring; 3) seeding the hot solution followed by cooling with vigorous stirring.

The third method gives the best fractionation. The second is better than the first.

When the third method is used, it is better to cool slowly than rapidly. When a large part of the rare earths is crystallized out (more than two-thirds in the crystallized fraction), fractionation is poor. Fractionation efficiency is better the lower the content of the Sa group elements in the cerite earths.

Fractional crystallization of the double magnesium nitrates by this method permits a rapid separation of Sa group elements from mixturesof cerite earths which are relatively poor in these elements.

Received May 13, 1954

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QUANTITATIVE DETERMINATION OF ALKYL-SUBSTITUTED 1-METHYL-4-PIPERIDONES

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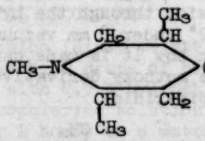
1,2,5-Trimethyl-4-piperidone —  — one of the alkyl-substituted γ-piperidones is of particular interest, since it is an intermediate in the synthesis of promedol, which is a new and effective anesthetic. Since, as far as we know from the literature, there is no method for the quantitative determination of 1,2,5-trimethyl-4-piperidone, we made the development of such a method our object. Since it is a base and at the same time has ketonic properties, 1,2,5-trimethyl-4-piperidone gives salts with acids and forms an oxime with hydroxylamine. We used these reactions for its quantitative determination. 1,2,5-Trimethyl-4-piperidone is easily titrated with both 0.1 and 0.5 N hydrochloric acid using bromocresol green (99.64%; 99.31%; 99.84%).

The correctness of our choice of indicator was confirmed by the fact that during potentiometric titrations the potential jump at the equivalence point corresponds with the color change of this indicator. Oxime formation also proceeds quantitatively under certain conditions.

We used a 5% hydroxylamine hydrochloride solution (for its preparation see below), which was added to our ketone after preliminary neutralization of the ketone with 0.5 N hydrochloric acid.

Oxime formation was carried out both in the cold and on heating for various periods. The hydrochloric acid formed during oxime formation was titrated with 0.5 N alkali to a color the same as that of a blank test.

Best results were obtained by heating at 80° for 2 hours. In the first experiments based on oxime formation, neutralization of 1,2,5-trimethyl-4-piperidone with hydrochloric acid was carried out (without indicator) using the same amount of 0.5 N hydrochloric acid as was used for titrating an equal aliquot of ketonic solution, but using bromocresol green.

In later experiments, in order to simplify the method we neutralized the same aliquot of ketone with 0.5 N hydrochloric acid, using bromocresol green as indicator, as was subsequently used for oxime formation. In this case exactly the same number of drops of bromocresol green was used for the blank as was used for the preliminary neutralization of the ketone.

When the hydrochloric acid which is liberated during oxime formation is titrated using bromophenol blue as indicator (when the ketone is neutralized by addition of the calculated amount of acid), there is a clear-cut color change at the equivalence point.

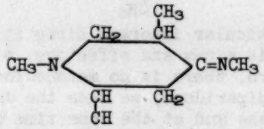
The substitution during this titration of bromophenol blue for bromocresol green when the ketone is neutralized beforehand to an indicator end point is

undesirable, since the color change is not so sharp. (The titration of the ketone itself with acid using bromophenol blue as indicator leads to a drawn-out color change). As a consequence, it is recommended that the hydrochloric acid should be titrated during the oxime reaction in the presence of two indicators: the results obtained are the same as with bromophenol blue alone.

E.g., 99.56%, 99.69%, 99.25% (for preliminary neutralization of ketone using the calculated amount of acid; titration of the hydrochloric acid formed during oxime formation was done in the presence of bromophenol blue).

99.29%, 99.19% (for preliminary neutralization of ketone using bromocresol green as indicator; the hydrochloric acid formed during oxime formation was titrated using bromocresol blue).

These methods were developed using 1,2,5-trimethyl-4-piperidone which had been purified by conversion through the hydrochloride, and by distillation. The material boiled at 70-72° under 8 mm vacuum. Technical 1,2,5-trimethyl-4-piperidone, depending on how it is made, can contain: neutral ketones (allyl-isopropyl ketone and the methoxy derivatives corresponding to it), and also 1,2,5-trimethyl-4-methyliminopiperidine.



1,2,5-Trimethyl-4-methylimini o piperidine was shown experimentally to titrate quantitatively with acid. It requires, however, two equivalents of acid and not one, since on hydrolysis it forms methylamine and 1,2,5-trimethyl-4-piperidone. The 1,2,5-trimethyl-4-piperidone thus formed undergoes the oxime reaction under the conditions indicated above. If, therefore, the above mentioned products are present in technical 1,2,5-trimethyl-4-piperidone, the latter is determined as follows:

An aliquot of the technical product is first titrated with acid using bromocresol green as indicator, the neutralized ketone is subsequently extracted with ether, while the residue after ether extraction is treated with hydroxylamine under the same conditions as used for pure 1,2,5-trimethyl-4-piperidone. The excess (mls) of hydrochloric acid used for preliminary neutralization of the technical product minus the amount (mls) of alkali used for neutralizing the hydrochloric acid liberated during oxime formation, multiplied by two, is equivalent to the amount of 1,2,5-trimethyl-4-methylimin o piperidine.

1,2,5-Trimethyl-4-piperidone is determined from the difference between the doubled amount (mls) of alkali used after oxime formation and the amount (mls) of hydrochloric acid used for neutralizing the aliquot.

Thus in a synthetic mixture consisting of 19.2% neutral ketones, 9.4% of 1,2,5-trimethyl-4-methyliminopiperidine, and 71.4% 1,2,5-trimethyl-4-piperidone, 70.2% of the latter and 9.5% of 1,2,5-trimethyl-4-methyliminopiperidine were found. This is quite a satisfactory result for a technical product.

On the assumption that the method developed for 1,2,5-trimethyl-4-piperidone is applicable to other alkyl-substituted 1-methyl-4-piperidones, we tried it out on 1,2,5-trimethyl-6-ethyl-4-piperidone[1] (b.p.. at 3 mm 77-79°) and got good results (see Table).

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[1] The 1,2,5-trimethyl-6-ethyl-4-piperidone, as well as the 1,2,5-trimethyl-4-methyliminopiperidine, were kindly given to us by V. A. Rudenko of the Institute of Organic Chemistry, Acad. Sci. USSR, for which we wish to thank him.

TABLE

Wt. of material, in g	Vol. of 0.5 N HCl used, in ml	Amount of 1,2,5-trimethyl-6-ethyl-4-piperidone (by titration with HCl) in %	Amount of 0.5 N NaOH used, in ml	Amount of 1,2,5-trimethyl-6-ethyl-4-piperidone (by oxime formation with 5% hydroxylamine) in %
0.5253	6.16	99.24	6.15	99.08
0.5371	6.31	99.42	6.32	99.58
0.5524	6.47	99.12	6.50	99.58
0.5562	6.53	99.35	6.55	99.66

EXPERIMENTAL PROCEDURE

a) 0.5-0.6 g of the pure preparation (exact weight) is measured out with a Lunge pipet into a 100 ml conical flask, 2 drops of bromocresol green are then added, and the solution titrated with 0.5 N hydrochloric acid to a yellow color. 25 ml of 5% hydroxylamine hydrochloride solution is then added, and the mixture heated under reflux at 80° for 2 hours on a water bath. The hydrochloric acid evolved is titrated with 0.5 N sodium hydroxide to a color equal to that of a blank carried out in parallel, containing exactly the same amount of hydroxylamine hydrochloride, indicator, water, acid and alkali as used for the sample itself.

b) 0.6-0.7 g of the technical product (exact weight) is measured out with a Lunge pipet into a 50 ml separating funnel, 2 drops of bromocresol green are added and the solution titrated with 0.5 N hydrochloric acid to a yellow color of the solution. The solution is then extracted twice with ether (in 15 ml lots). The aqueous solution is run off into a 100 ml conical flask, the ether solution is washed twice with water in 5 ml lots, and the wash water added to the total aqueous extract. Subsequent procedure is the same as for the pure compound.

The percentage content of 1-methyl-4-piperidone is calculated from the formula:

$$\frac{(2b - a)\cdot M\cdot 100}{2\cdot 1000\cdot K} = \% \text{ content},$$

where b is the amount of 0.5 N sodium hydroxide used for titrating the acid after oxime formation (in mls); a is the amount of 0.5 N hydrochloric acid used for titrating the aliquot (in mls); M – the molecular weight of the substituted γ-piperidone; K – weight of aliquot, in g.

The percentage content of alkyl-substituted 1-methyl-4-methyliminopiperidine is calculated from the formula:

$$\frac{(a - b)\cdot 2\cdot M\cdot 100}{2\cdot 1000\cdot K} = \% \text{ content}$$

The legends are the same as above.

Preparation of 5% Hydroxylamine Hydrochloride. 50 g of hydroxylamine hydrochloride is dissolved in 90 ml of water at 80-90° (if the solution is turbid, it should be filtered). 300 ml of alcohol and 6 ml of bromophenol blue indicator are added. The solution is neutralized with alcoholic alkali to a bottle-green color, when it is made up to a liter with alcohol.

Preparation of Bromophenol Blue Solution. 0.4 g of indicator is dissolved in 10 ml of 0.1 N sodium hydroxide and diluted with water to 100 ml.

SUMMARY

1. Methods are described for the quantitative determination of pure alkyl-substituted 1-methyl-4-piperidones: a) by titration with hydrochloric acid using bromocresol green as indicator; b) by oxime formation after neutralization with hydrochloric acid.

2. A method is given for the quantitative determination of alkyl-substituted 1-methyl-4-piperidones and alkyl-substituted 1-methyl-4-methyliminopiperidines in the technical product.

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COLOR REACTION OF COMPLEX FORMATION BETWEEN ELEOSTEARIC ACID AND PICRIC ACID AS A QUALITATIVE TEST FOR TUNG OIL

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The capacity of highly nitrated organic compounds to react in virtue of their non-valency forces with multiple carbon bonds has been known for a long time [1,2]. A characteristic example of such a reaction is that of tetranitromethane to give colored complexes with almost all carbon compounds having multiple bonds.

Of special interest from this point of view is picric acid which, thanks to its capacity of forming complexes with aromatic compounds, has found wide application for the identification of the latter [1]. These reactions of picric acid are very often color reactions and in individual cases have been used as color tests [3,4].

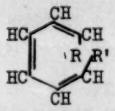
Picric acid can only form complexes with aromatic hydrocarbons, and amines and their derivatives. The only exception is pinene picrate. A method of separating aromatic hydrocarbons from other compounds is based on this fact [1,2].

Results are often given in the literature of color reactions of picric acid with other compounds containing ketonic and aldehyde groups, carbohydrates, glucosides, etc., which, however, do not belong to the aromatics but are more often representative of aliphatic or hydroaromatic compounds. It should be noted that all these color reactions [5,6,7] are carried out between the types of compounds just mentioned and picric acid in a solution of the alkali salts of the latter. In so far as is known the picric acid itself in alkaline media gives colored compounds of the nitron acid type [2]; all the color reactions are not really the result of direct interaction between picric acid and test material, but are simply an intensification of the color reaction between alkali and picric acid. In view of the instability of these intensification processes, their application as colorimetric methods is restricted. In order to avoid such difficulties during a study of the reaction between picric acid and the compounds we were interested in, the reactions were all carried out in acid or neutral media.

In studying the properties of eleostearic acid, we reckoned that picric acid, just like other nitro compounds, should, under certain conditions, react to varying degrees to form complex compounds not only with the multiple bonds of aromatic hydrocarbons, but also with screened multiple bonds and with any carbon multiple bond.

This is more than probable in the case of eleostearic acid, since in certain cases the conjugated double bonds of this acid in solution may not only be stretched out in a zig-zag fashion along a straight line, but may be twisted into a spiral [8].

This twisted arrangement of the carbon atoms in the molecule of eleostearic acid with conjugated double bonds can be represented as follows:



$R = -(CH_2)_3CH_3$

$R' = -(CH_2)_7COOH$

In some cases 6 of the carbon atoms of eleostearic acid with conjugated double bonds may have a spatial configuration – not related, of course, to their other configurations – and, consequently be in a general electrodynamic state [9,10] very similar to that in such aromatic compounds as give picrates. This fact is probably one of the major reasons for a non-valency interaction between picric acid and eleostearic acid.

We found that like many other compounds, picric acid in solution in acetic acid, ether, acetone, dichloroethane, etc., reacts even at room temperature with eleostearic acid – an aliphatic compound. This is confirmed by the appearance of a garnet -red color.

Experiments on intensifying this reaction by adding anhydrous salts to the reaction media: sodium and mercuric acetate, and also anhydrous cupric and ferric sulfates, did not give positive results.

It was subsequently shown that a similar color reaction also occurs when picric acid reacts with an acetic acid solution of eleostearic acid in the initial stages of polymerization. It was also observed when eleostearic acid was fused with picric acid, and on melting eleostearic acid in hot saturated aqueous solutions of picric acid. A rather curious phenomenon was observed in this case, viz., a change in color of the picrates formed. On removal of the solvents listed above, or on cooling the fused picrates to room temperature, their color changed from a garnet-red to a light yellow; they regained their garnet-red color on dissolving them in the same solvents or on heating them. Thus both the solvents we used as well as heat can intensify the color.

Eleostearic acid was isolated from the picrates formed by treating the latter with aqueous ammonia. This led us to conclude that these picrates are molecular compounds of a complex type.

Analyses of these complexes showed that in contrast to the aromatic hydrocarbons which form complexes with picric acid in the ratio 1:1, eleostearic acid complexes with picric acid in the ratios 10:1, 5:1, and 3:5. The melting points of these complexes are not sharp and vary within the limits 68-70°.

It was shown experimentally that the changes in color intensity of the compounds formed between picric acid and eleostearic acid do not follow Beer's law, and that the sensitivity of a method based on this reaction is 91 mg/2 ml.

We did not use this reaction therefore for colorimetric determination of eleostearic acid. This reaction however can be used under certain conditions as a qualitative test for this acid.

Picrates of aliphatic compounds (apart from various amines) have not hitherto been described, nor a color reaction between picric acid and aliphatic compounds. This reaction of eleostearic acid with picric acid, therefore, can be regarded as the first example thus far described of a reaction between picric acid and an aliphatic compound, and also the first instance of a color reaction between picric acid and an aliphatic compound.

Tung oil, which sometimes contains 80% eleostearic acid, is completely analogous in behavior to eleostearic acid with respect to its reaction with picric acid. This is very interesting from a practical point of view, since in general there is no color test known for tung oil. The two qualitative but non-color

reactions for tung oil are based on [11, 12] it capacity to gelatinize on simple heating, or according to Marcuson, on the reaction of its ether solution with ferric chloride. These reactions, however, cannot be used for detecting tung oil in the presence of other oils if there is less than 10% of tung oil present in the mixture [13]. It is possible to work out a colorimetric method for tung oil in a mixture with other oils by using a reaction discovered in 1919, viz., diazotization of diene hydrocarbons [14]. This reaction was successfully used by A. P. Terentyev both as a qualitative test for diene hydrocarbons with conjugated double bonds [15, 16], and for the qualitative detection of eleostearic acid in tung oil [17].

We have worked out a colorimetric method by means of which tung oil can be determined in the presence of other plant and animal oils when the tung oil content is not less than 1%. The existing method [3] of detecting mineral oils in plant oils, which is based on adding a benzene solution of picric acid to the test material, is not specific for mineral oils since the possible presence of tung oil in the mixture is overlooked.

EXPERIMENTAL

1. Preparation of Starting Materials.

a) Eleostearic Acid. 100.0 g of tung oil was dissolved in 300.0 ml of 10% alcoholic NaOH and the mixture heated on a water bath under reflux for 6.5 hours. While still hot, the thick transparent mass was transferred to a beaker and 1 liter of water and 400 g NaCl added. The soap layer on the surface was worked up a few times with saturated aqueous NaCl. The soap obtained was dissolved in the smallest possible amount of alcohol by heating. This solution while still warm was neutralized with 10% H_2SO_4 to a weak acid reaction (litmus). The mixture of fatty acids which separated out on the surface was an oily layer, which on cooling formed a solid mass which was removed from the aqueous solution. The mass obtained, which had the specific tung oil odor, was treated with water a few times until it gave a neutral reaction to litmus. The mass was then crystallized a few times from dilute aqueous alcohol according to the current method [13], the solution being cooled in an ice-salt mixture. After suction filtration on a filter funnel the eleostearic acid had a melting point of 61-63°.

In order to convert the α-isomer into the β-isomer, this mass of crystals was dissolved in 400 ml of 60% alcohol and boiled under reflux for 6 hours. After cooling it was recrystallized in the cold using an ice-salt mixture for cooling. The crystals after suction filtration had a melting point of 69-70.5° and after repeated crystallization, 71-72°.

b) An aqueous solution of picric acid saturated with the latter at 70° was prepared by heating excess picric acid with water at 80° and filtering the hot solution at 70°.

c) An aqueous solution of picric acid saturated with the latter at room temperature (18°) was prepared by cooling solution (b) to room temperature and filtering the cooled solution.

d) A saturated solution of picric acid in acetic acid was made by cooling a boiling saturated solution of picric acid in acetic acid to room temperature and filtering.

2. Color Reaction of Eleostearic Acid and a Color Test for Tung Oil

2.0 ml lots of acetic acid saturated with picric acid at room temperature were placed in 3 test tubes. 0.2 g of eleostearic acid was added to the first, an equal amount of eleostearic acid in its initial polymerization stages to the second, and 5 drops of tung oil to the third.

After shaking tubes and contents for 1/2 minute at room temperature, the mixtures in all three test tubes acquired an intense garnet-red color.

Similar color changes occurred when, instead of the acetic acid solution saturated with picric acid at room temperature, saturated solutions at room temperature of picric acid in acetone, ether, benzene, butanol and dichloroethane were used.

The sensitivity is 91 mg/2 ml.

3. A Color Test for Tung Oil in the Presence of Other Oils.

Test solutions of 1,2,5, and 10% of tung oil in sunflower oil were made. Similar solutions of tung oil in soya and linseed oils respectively were also made; 12 solutions in all.

15 drops of these 12 samples were placed in test tubes and 2.0 ml of acetic acid saturated with picric acid at room temperature added to each.

The controls were test tubes containing pure sunflower, soya and linseed oils, respectively, to which the same amount of the picric acid-acetic acid solution had been added.

The following changes were observed after shaking the test tubes for 2-3 minutes at room temperature. After 30 minutes a layer of oil floated on the surface of the glacial acetic acid. A weak orange color could be detected in the oil layer for a 1% concentration of tung oil. This color was stronger when 2% was present in the oily layer floating on the surface; no color change was observed in the oil layer in the control tests.

4. Complex Compounds of Eleostearic Acid with Picric Acid

a) 250 ml of water saturated with picric acid at 70° was placed in a beaker and 5.0 g of eleostearic acid added (m.p . 71-72°). The beaker was placed on a boiling water bath and the mixture mixed thoroughly, the temperature was allowed to reach 80°; when the beaker was removed from the bath, an oily mass of a garnet-red color formed on the surface of the solution. The mixture was stirred until the temperature reached 60°, when it was allowed to cool to room temperature. The red oily liquid floating on the surface changed into a light yellow solid mass on cooling. This was separated from the liquid with a porcelain spatula and placed in a porcelain mortar. The mass was carefully triturated 2-3 times with water saturated with picric acid at room temperature, ca. 20 ml of solution being used each time.

The triturated mass was washed with 20 ml of the same aqueous picric acid solution and then with 50 ml distilled water. The washed precipitate was finally dried between sheets of filter paper and in a desiccator over $CaCl_2$.

The light yellow product obtained turned garnet-red in color on fusing but regained the light yellow color on cooling; m.pt. 68-70°.

Found %: C 74.34, 74.29; H 10.03, 10.27; N 1.30, 1.45
Calculated %: C 74.13; H 10.13; N 1.39

$$(C_{18}H_{30}O_2)_{10}[(NO_2)_3C_6H_2OH] = C_{186}H_{303}O_{27}N_3$$

b) 13.5 g of eleostearic acid and 9.0 g of picric acid were placed in a test tube which was then immersed in a water bath to the level of the reaction mass inside the tube. On heating to 70-90° the whole melted and changed into a garnet-red liquid. The liquid was maintained at this temperature for 10 minutes and stirred with a thermometer. The liquid was then allowed to stand at 90° for 3 minutes without stirring. The test tube was removed from the bath and allowed to cool to room temperature. When this was done, the formation of two separate layers was observed, the upper one a transparent red layer and the lower an opaque red layer. On cooling to room temperature the color of both layers changed from a yellowish-red to a pale yellow. The test tube was carefully cut at the junction of the two layers and the two parts separated.

The m.p. of both layers was 68-70.5°.

The lower layer analyzed as follows:

Found %: C 50.01, 50.55, 51.14; H 5.46, 5.54, 5.52; N 10.54, 10.58
Calculated %: C 50.94; H 5.34; N 10.61.

$(C_{18}H_{30}O_2)_3[(NO_2)_3C_6H_2OH]_5 = C_{96}H_{105}O_{41}N_{15}$

While the analysis for the upper part was:

Found %: C 71.25, 71.34; H 9.75, 9.57; N 2.47, 2.70
Calculated %: C 71.12; H 9.51; N 2.59

$(C_{18}H_{30}O_2)_5[(NO_2)_3C_6H_2OH] = C_{96}H_{153}O_{17}N_3$

A small amount of the two layers and some pure eleostearic acid, respectively, ground to a fine powder were spread in fine layers on watch glasses and allowed to stand in air at room temperature. After 3 days the eleostearic acid had polymerized, while the others remained in their powder form (to the hand).

5. Decomposition of the Complexes and Isolation of Eleostearic Acid

0.5 g of the material described in section (a) of 4 was heated at 50° to dissolve it in 150 ml concentrated ammonia. The solution was diluted with an equal volume of water and neutralized with 10% H_2SO_4 to a weak acid reaction. The solid mass which separated out was filtered off and washed with cold water until the wash water was no longer colored yellow. The precipitate was then passed through the same sequence of operations again.

The precipitate obtained after repeated crystallization from methanol and ether formed flat crystals with a m.p. of 69-71°. These crystals did not depress the m.p. of eleostearic acid, the mixed m.p. was 69-72°.

Similar results were obtained when both upper and lower layers from 4(b) were given the same treatment.

SUMMARY

1. Eleostearic acid gives a color reaction with picric acid.

2. A method has been worked out for the colorimetric detection of eleostearic acid and color tests for tung oil, both on its own and mixed with other oils developed. 1% tung oil can be detected in the presence of other oils.

3. Complex molecular compounds of eleostearic acid of the following composition have been isolated:

$(C_{18}H_{30}O_2)_{10}[(NO_2)_3C_6H_2OH]$; $(C_{18}H_{30}O_2)_5[(NO_2)_3C_6H_2OH]$;
$(C_{18}H_{30}O_2)_3[(NO_2)_3C_6H_2OH]_5$.

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CRITICISM

B. P. Nadeinsky. "Introduction to Analytical Chemistry," Moscow, Soviet Science, 1953, 364 pp. Printing 10,000. Price, 7 rubles 70 kopeks.

Soviet literature on analytical chemistry has been enriched by B. P. Nadeinsky's interesting book. As indicated in the foreword of the book, the theoretical foundations and calculations of analytical chemistry are considered. Textbooks which have been devoted exclusively to the theoretical questions of qualitative analysis have been in existence for a long time.

The book has a short introduction on the role of analytical chemistry and analytical methods: the book is divided into 11 chapters, in which the most important theoretical questions are discussed. At the beginning the author gives a brief review of the development of analytical chemistry in Russia, and also gives a short list of papers at the end of the chapter (only Soviet authors). This is useful to the reader, particularly students who want to know something about some of the outstanding achievements of Russian analysts and about the development of the theory and of new methods in analytical chemistry.

The second chapter, "Analytical Classification of Cations and the D. I. Mendeleev Periodic System," in contrast to those in many other textbooks, makes it quite clear that the division of cations into groups is not artificial, but is intimately connected with the periodic law.

In succeeding chapters chemical equilibria in analytical reactions, methods of expressing solution concentrations, and calculations of the concentration and activities of protons in solution are discussed. Separate chapters are devoted to hydrolytic processes, equilibria between solutions and precipitates, and also to oxidation-reduction reactions, complex compounds, and colloids in analytical chemistry. The book ends with a useful chapter on the sensitivity and specificity of analytical reactions.

In comparison with other books the material on buffer mixtures, equilibria between two precipitates in solution, and theory of precipitation by hydrogen sulfide is set out better; many good examples are adduced in dealing with these questions and with some others.

It is peculiar, therefore, that the most important question of the degree of electrolytic dissociation, on which all this depends, is not discussed; the solubility of sparingly soluble electrolytes is discussed in a niggardly fashion. It is not made clear on what factors the rate of chemical reactions is dependent, nor is anything said about ion solvation, and there is no clear explanation why strong electrolytes dissociate completely into ions. The subject of systems in equilibrium is barely touched upon, and no mathematical expression of the law of mass action is given. Unfortunately, throughout the whole book, in discussing analytical reactions, there is no indication that the reaction tends to follow the path whereby material with a lower concentration of ions in solution is formed.

We think that the title, "Introduction to Analytical Chemistry," does not define exactly the material set forth in this book. In effect the author has only considered the theoretical basis and related calculations.

The book is replete with numerous examples and problems which are treated in detail. Many of them are very important and are of very decided interest. True, Nadeinsky seems to be attracted more to solving these problems and is apt to forget to expound the principles on which they are based. Some chapters, particularly 5 and 6, are overloaded with examples which do not have any

direct bearing on the questions of qualitative analysis under discussion, but tend to obscure the chemical meaning of the processes and do not support the theoretical positions of the book. This is true, e.g., of the determination of the ionic composition of solutions of tri-basic acids (see p. 135). As an example of overloading the book with solutions of various problems, we may quote the excessive number of examples and detailed calculations of the molality of solutions which are rarely used (see pp. 82, 83, etc.). The activity of H^+ and OH^- ions in solutions of weak bases and acids is not clearly explained. These sections again are cluttered up with complex problems which are practically incomprehensible to students (see pp. 106-128). The number of problems could be reduced and their solutions simplified.

In general, there is quite a number of unfortunate or unnecessary choices of examples; e.g., No. 5, p. 64, the calculation on p. 170, example 6, p. 206, example 5, p. 236. No. 7, p. 228, cannot be solved if only the data available in the book are used. On the other hand, there are only a few examples on the important question of buffers in qualitative analysis.

The random nature in which the author has arranged his material is apparent in Chapter 6 on salt hydrolysis. The very concept of this important process and different instances of it are given only a brief treatment (see pp. 162-163). A large part of the chapter is devoted (pp. 165-200) to calculations of hydrolysis complicated by other processes. In addition, there is no information on such important practical examples as, say, the action of $(NH_4)_2S$ or Na_2CO_3 on Al^{3+} or Cr^{3+} ions. It would have been more expedient to explain the impossibility of forming, e.g., Al_2S_3 in aqueous solution; even in this case the author overlooks the chance of using simpler examples which are also of practical importance, in favor of examples which are not only more complicated but of little importance. For some unaccountable reason, formation of basic salts as a result of hydrolysis is not discussed in this chapter.

Chapter 9 on oxidation-reduction reactions was written in conjunction with G. E. Levant and is well written. It is a pity that the close relation between these processes and the Mendeleev periodic law is not shown. These reactions are not classified. In a review of the most important oxidizing agents, such important compounds as oxygen, MnO_2, concentrated sulfuric acid, and ferricyanide, have been omitted. A number of reducing agents has also been left out, and nothing is said about electric currents. While on p. 46, NO_2 is regarded as an oxidizing agent, on p. 287 this is correctly refuted. There it is emphasized that NO_2 possesses both oxidizing and reducing properties. It should have been explained how to change over from ionic equations to equations expressing reactions in molecular forms. There are no examples to explain oxidation-reduction reactions, e.g., solution of arsenic sulfide in nitric acid and reactions for complex and organic compounds.

The short chapter on colloids in analytical chemistry, which takes less than 9 pages, should be expanded. The position of colloid particles in dispersed systems should be demonstrated and their comparative sizes given. No emphasis is laid on an important fact in analytical chemistry – the formation of colloidal particles as an intermediate stage during all reactions involving preparation and solution of precipitates. Neither is anything said about "protective colloids," hydrophilic and hydrophobic, or about the significance of adsorption, which plays an important part in analytical chemistry. As against the usual custom, the author does not emphasize the importance of work carried out by Soviet scientists.

We should like to dwell here on an important methodological question, which from one point of view has not been solved satisfactorily in most textbooks. Should chemical equations be written with an equals sign or with an arrow?

Unfortunately the same author may, in the course of his own book, use both

conventions. B. P. Nadeinsky does this; e.g., the equation for the hydrolysis for ammonium acetate. On p. 164 this equation is written with an arrow while on p. 189 the identical equation is written with an equals sign. This is not a printer's error. It occurs over and over again and not only in Nadeinsky's book. There seems to be no logic about it at all. On p. 128 the electrolytic dissociation of sulfuric acid is written down as a two-stage process, the first stage with an equals sign and the second stage with the arrow sign. The number of such examples is countless.

How one should write chemical equations is not simply a matter of form. An equation should indicate the direction of a process and convey information. We are of the opinion that in general equals signs should not be used, since it senselessly equates reaction product with reactants. A chemical equation does not necessarily signify one reaction, and the reactants and reaction products cannot be dealt with like mathematical quantities. The weights of reactant and reaction products may be balanced, but at the same time important energy changes are taking place. Dropping the equals sign in no way destroys the validity of Lomonosov's law.

Substitution of an arrow for the equals sign immediately indicates the path of a reaction. The qualitative difference between materials found on the left and right-hand sides of a chemical equation follows from the very definition of the word "chemistry" itself. Two arrows $\rightleftharpoons$ should of course only be used for indicating completely reversible reactions. Nadeinsky is therefore wrong when he writes the electrolytic dissociation of water and tens of other reactions with two arrows of equal size.

For textbooks, particularly on analytical chemistry, the use of an arrow is of great methodological importance. In equations which represent reactions that go practically to completion (such reactions are the ones of greatest interest to analysts) one arrow alone should be used $\longrightarrow$. When reversible reactions occur, and it is desired to indicate the overall direction of the process, it is best to use two arrows differing in length $\rightleftharpoons$. Such a method explains the chemical meaning of a reaction more clearly.

The chapter on complex compounds is weak. The general bases concerning the composition and structure of these compounds are not pointed out and their great importance in analytical chemistry is not brought out convincingly enough. Some of the examples are unfortunate. On p. 45 it is written that excess reagent forms $Na[Ag(S_2O_3)]$ and $Na_2[Cu_2(S_2O_3)_2]$. This is not true; $Na_3[Ag(S_2O_3)_2]$ and $Na_3[Cu(S_2O_3)_2]$ are formed. The equations on p. 243 are for some reason printed in the reverse order. When cobalt and silver complexes of ammonia decompose in aqueous solution, ammonia is not formed, etc.

In a chapter on complex compounds, it would be desirable to give some information on coordination bonds, donors, and acceptors. Little is said about halogenoids and nothing about poly-acids, which are important in qualitative analysis. The author daringly affirms that "during complex formation, there is as a rule a sharp change of color" (see p. 242). There are numerous examples which do not confirm this.

The formation of $[Co(CN)_6]^{4-}$ (see p. 259) cannot be recommended as an example without a warning about the extreme instability of cobalticyanides. Otherwise the reader may get the impression that the method given by the author for the preparation of these ions is very simple.

The great drawback of the book is the absence of a theoretical treatment of physico-chemical analytical methods. In particular, there is no description of chromatographic methods, which are being used so successfully in analysis.

We should like to make some further special points. Chapter 5 has a large section on acid salts, but nothing about basic salts. In the section on indica-

tors, which is not so well written as the others, one would expect a modern definition of an indicator. In general, the theory of indicators is not considered.

There are errors in the description of precipitation of Group V cations (see p. 41). For many reasons the group's reagent should be used not on its own, but together with a small amount of ammonium salts, and in the presence of ammonia if insufficient ammonium salts are present.

It is stated on p. 225 that "the hydroxides of chromium and aluminum are more insoluble than their sulfides because the Cr^{3+} and Al^{3+} cations are precipitated as $Cr(OH)_3$ and $Al(OH)_3$." It is not a question of the lowest solubility but of the hydrolysis of the sulfides.

The author's statement (p. 70) re the equation $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ is not clear.

If the word dissociation is to be used, then it should be made clear what sort of dissociation is meant – thermal or electrolytic. Wouldn't it be better to say "ionization" instead of "electrolytic dissociation."

When the word soda is used it should be stated whether it is carbonate or bicarbonate. It is best to use chemical names.

In discussing Lomonosov's work in forming the first laboratory in Russia, reference should be made to his struggle with Shumakher and his pro-German reactionary group.

Among the portraits there is none of T. E. Lovits.

There is no subject index. The author repeats himself quite often, even on the same page.

There are a number of typographical errors.

All these drawbacks lower the value of the book.

We should like to see a new edition of this book free from all the drawbacks.

O. K. Dobrolyubsky.

May 8, 1954

Publishers note: Several paragraphs dealing with Russian grammar and spelling, violations of which in the book being reviewed are noted, have been omitted from this translation.

NEW REAGENTS

The All-Union Research Institute on Chemical Reagents wishes to inform all organizations and universities occupied with the application and testing of organic reagents for cations that the Institute has synthesized a new, highly sensitive organic reagent for the colorimetric determination of beryllium – "BERILLON II IREA."

Organizations and universities wishing to test the new reagent can get free samples and instructions for its use if they apply to the Institute's address (Moscow, Zh-33, Samokatnaya Ulitsa., D. 4.).

The production of the new reagent is not yet on a factory scale and in order to have an idea whether it is worth organizing its production on such a scale, all those who get samples of BERILLON II IREA are requested, within three months from the date of receipt of sample, to give the Institute some idea of their future requirements.

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OSCILLOGRAPHIC POLAROGRAPHY

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In recent years a new technique has been developed in polarographic analysis, in which an oscillograph is used for recording the polarographic currents. The method which has developed along this new direction has been called oscillographic polarography. With the development of oscillographic polarography even greater possibilities have been opened up to the technique of polarography; many processes which occur at high speed on the dropping mercury electrode are now within the scope of study, while it has become possible to determine electrode reaction rates and their reversibility.

Oscillographic polarography permits determination of the charging point during the growth of a drop and the capacity of the double electrical layer on the boundary of separation, mercury-solution. These are possible as a result of the recording on the cathode ray screens of oscillographic curves which reflect the processes occurring on the dropping mercury electrode during rapid potential changes on the electrodes of the polarographic cell.

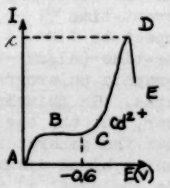

Fig. 1. Oscillograph curve for cadmium.

The principle of the method is simple: a voltage which is proportional to that applied to the polarographic cell is applied to the plate which deflects the cathode ray of the oscillograph in a horizontal direction, while a voltage proportional to the current flowing through the electrolytic cell is applied to the plate deflecting the cathode ray in a vertical direction. A current-voltage curve is thereby obtained on the screen. When a saw-toothed voltage is applied to the cell electrodes, the form of the curves is that shown in Fig. 1. It is possible to determine what particular element is in solution from the value of the voltage at which there is a sudden increase in current flowing through the cell (Point C). A further increase in voltage across the cell after passing the reduction potential (or oxidation potential) for a particular substance leads to an increase in the current flowing through the cell to some definite maximum value. From the maximum value for the current (Point G) it is possible to determine the amount of test material in solution.

Some of the apparatus described below permit determinations to be made to an accuracy of up to 1%. Measurement of currents of the order of 10^{-2} μA means that micro determinations can be carried out.

First and second order maxima /1/, which interfere with quantitative analysis, appear on the current-voltage curves when using conventional polarography. In order to suppress these maxima the technique usually employed is to add surface active agents; these however tend to inhibit the electrochemical processes and give rise to " spurious" polarographic curves /2/. Maxima are absent in oscillographic polarography because the surface of the mercury drop is stationary while one impulse is being applied. There is therefore no need to add surface active agents when this technique is used.

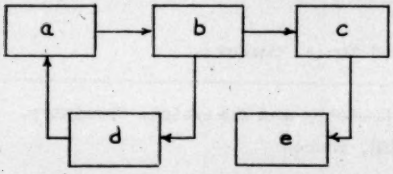

Fig. 2 Block Scheme of an Oscillographic Polarograph
a) Generator, b) polarographic cell, c) current or voltage amplifier, d) synchronizing system, e) oscillograph

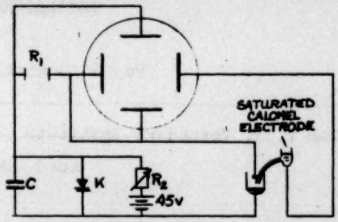

Fig. 3. Matheson and Nichol's Oscillographic Polarograph.

The type of oscillographic curve obtained depends on the set-up used; thus the following types of curves have been obtained by various authors: current-time (I—t), potential-time (E—t), differential-of-voltage-with respect-to-time— time (dE/dt—t), differential of current with respect to time-time (dI/dT—t). Nearly every one of the papers published on oscillographic polarography contains details of original oscillographic polarographs. In principle all the various set-ups differ very little from each other, but the basic set-up determines the potentialities of the instrument: the generator, the amplifier, and various synchronizing systems. A general block diagram of an oscillographic polarograph is shown in Fig. 2. This includes: 1) a generator of impulses of definite shape, amplitude, frequency, and duration; 2) the polarographic cell (with possibly a calomel electrode); 3) an amplifier for current or voltage according to the frequency of the impulses applied to the cell; 4) a synchronizing system, designed for synchronizing the frequency of the impulses applied to the cell with the drop time of the electrode; 5) a normal oscilloscope or a specially constructed oscilloscope designed for reproducing oscillographic curves. Recording on the screen is usually photographic (possibly even visually).

I. Original Blocks (Circuits) for Oscillographic Polarographs.

In this review we have considered it expedient only to discuss the most interesting and original blocks (circuits) published for the construction of oscillographic polarographs. The radiotechnical schemes adduced below are simplified variants of the original circuits proposed by the authors of the articles discussed.

Matheson and Nichols /3/ were apparently the first to get the idea of using a cathode ray tube in polarography. They were attracted by the convenience and rapidity with which oscillographic curves of I—E could be registered by this new technique. They used an alternating sinusoidal voltage from a circuit with an amplitude of 1.5 V on top of a constant voltage of 1.5 V.

Thus a change in potential of from 0 to 3 occurs at a frequency of 60 c.p. The current flowing through the cell on passing through an external resistance causes a drop in potential across the resistor which is then applied after amplification to the vertical plates of the oscillograph. The vertical deflection of the cathode ray is proportional to the current flowing through the cell.

The ray is swept horizontally by means of a sinusoidal voltage of the same frequency. A current-voltage curve is accordingly obtained on the screen. Reproduction of the oscillogram is achieved by synchronizing drop time with sweep frequency (60 drops/sec.).

Another variant was suggested by the same authors in which a linearly increasing voltage of 0 – 2.4 V was applied to the cell; this was supplied from a condenser charging through a variable resistance from a battery. The voltage was applied periodically by closing the condenser 30 times a second by means of an electric motor (Fig. 3).

Matheson and Nichols obtained a current-voltage curve of the type shown in Fig. 4 in which the drop time of 1/30 sec.; was accurately synchronized with voltage impulses of 30 cycles per second. When this method is used only one trace per drop is obtained and the current-voltage curve obtained on the visible screen is in the form of a stationary image.

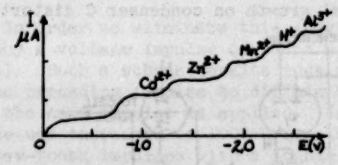

Fig. 4. Oscillogram for 0.1 N LiCl containing Cd^{2+}, Zn^{2+}, Mn^{2+}, Al^{3+}

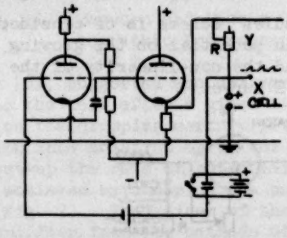

Fig.5 Schematic diagram of the Randles Generator

The authors found that the I – E curve was very similar to the current-voltage curves obtained by means of the ordinary method but the diffusion durrent was not strictly proportional to concentration. The half-wave potentials on Fig. 4 are slightly more negative than those obtained when using ordinary polarography.

This work despite its limitation is of interest because it demonstrated the possibility of using the oscillograph for polarographic studies. Matheson and Nichol's work showed that a change in potential drop on the load resistance has an essential effect on the nature of the curves.

Much later, Randles [4], proposed a new set-up in which this snag was eliminated and in which considerable improvements were made in the oscillographic method.

In set-ups constructed on the basis of the system suggested by Matheson and Nichols the error in the measured values of the current is determined by the ratio R/R_i (where R is the load resistance, R_i – the internal cell resistance) and increases with the latter.

A simplified Randles set-up is depicted in Fig. 5.

In such a system any change in the potential drop across the load resistor R alters the potential differences applied to the cell by 0.5% of the value of the change in the potential drop across R. This is achieved by using a cathode repeater with a return communication. The potential across the polarographic cell is supplied from a condenser C charging through a variable resistance from a battery. The frequency of the voltage change is altered step-wise by varying the resistance through which the condenser is charged. In this way a rate of potential increase across the cell of 0.14 to 0.88 V/sec can be obtained.

The increase in potential applied to the cell is synchronized with the fall of a drop and started after a given time interval (0.5-7 sec) after the fall of a drop. Such a delay in applying the potential permits an I – E curve to be recorded for any size of drop. This is ensured by incorporating in one of the anodes a univibrator relay which, at the fall of a drop, short-circuits a condenser C during the delay time and opens it for the time during which the potential applied to the cell increases. Delay time is regulated by changing RC in the univibrator circuit and corresponds to the duration of its impulse. If it is necessary to take several I – E curves corresponding to various drop sizes, then the univibrator is changed over for a multi-vibrator. To record weak currents passing through the cell on the screen a current amplifier is used which has variable amplification. The current voltage curve is of the type shown in Fig. 1.

Randles' scheme is of considerable interest although such a slow increase in potential on the growing drop (a tenth of the growing period of the drop) and the non-linearity of the potential growth on condenser C distort the I – E curve.

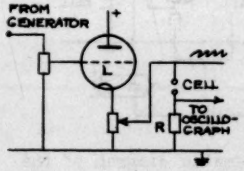

Fig. 6. The Delahay scheme (I)

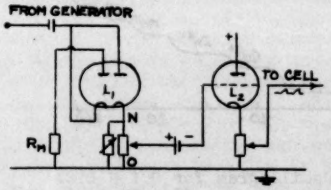

Fig. 7. The Delahay scheme (II).

These drawbacks were overcome a little later by Delahay [5]. Delahay got oscillographic curves of I – E by applying a saw-tooth voltage to a cell with a load resistor R. A simple generator operating on a thyratron was used to get the saw-tooth voltage. The saw-tooth voltage from the generator is applied through a divider (potentiometer) to the current amplifier, from the cathode of which the voltage of required amplitude and frequency is applied to the cell (Fig. 6).

The potential drop across a resistance R connected in series with the cell provides the polarographic current I to be recorded. This potential drop IR is amplified and applied to the vertical plates of the oscillograph. The vertical displacement of the ray is accordingly proportional to the current recorded. The horizontal displacement of the ray is proportional to the voltage applied to the cell; the horizontal sweep of the cathode ray is produced by directly applying a saw-tooth voltage of 160-180 V from the generator to the horizontal plates of the oscillograph. In this set-up therefore, the constant voltage applied to the cell is regulated as well as the voltage frequency and amplitude. The rate at which the potential applied to the cell increases can be as high as 100 V/sec. With such a high rate of potential increase it is

possible to record I–E curves corresponding to different drop sizes and to follow certain rapidly occurring electrode processes.

The drawback of this scheme is that the next voltage increase applied to the cell starts immediately after the sudden drop of the preceding impulse, i.e., at a moment when the ions reduced on the dropping mercury electrode have not succeeded in being completely oxidized and diffuse back into solution. This effect leads to a decrease in the maximum current from its true value particularly at the beginning of the oscillographic curve (i.e. for low cell voltages).

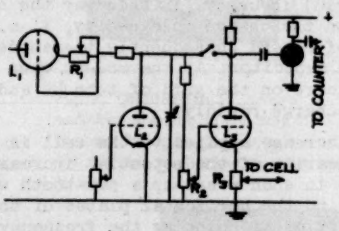

Fig. 8. The G. E. O. Kh. L Oscillographic Polarograph

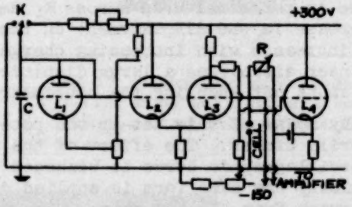

Fig. 11. Snowden and Page's Oscillographic Polarograph

In order to eliminate this snag Delahay [6], suggested another variant whereby a voltage impulse could be applied to the cell after a given time interval. Such a scheme permits ions reduced on the dropping mercury cathode by the preceding impulse to diffuse back again into solution up to the time when the next impulse is applied. In this set-up the rate of potential increase was increased to 1000 V/sec. This is achieved by chopping the base of the saw-tooth impulses with a double diode (Fig. 7). The apices of the saw-tooth impulses are applied to the voltage amplifier, from the cathode of which impulses of the requisite duration and amplitude are applied to the cell as before. The shape of the voltage depends on the value of the ratio R_M/R_{NO}. At $R_M/R_{NO} = 1$, the duration of a saw-tooth impulse is equal to the interval between them. For $R_M = 0$, this set-up gives the usual saw-tooth wave and operates like the previous set-up. Both set-ups permit several waves to be photographed during the time of growth of one drop; these waves give a complete picture of of the processes occurring on the growing drop.

The set-up which the authors of the present review [7], constructed is a modified Delahay circuit; by means of our apparatus it is possible to carry out quantitative determinations for the same rate of change of the saw-tooth voltage (Fig. 8).

The circuit is composed of several cascades with varying functions: 1) a saw-tooth voltage generator; 2) an amplifier for the saw-tooth voltage applied to the electrolytic cell; 3) an amplifier for the current flowing through the polarographic cell; 4) a source of supply (for anode voltage and filament heating); 5) a mechanical counter for recording the number of sweeps per unit time.

A generator based on a thyratron was used as a saw-tooth voltage supply; a variable capacitor and high resistance were coupled in parallel with this generator.

The capacitor was charged through tube L_1 which gives rise to an increasing

voltage on the thyratron anode. When the voltage on the thyratron anode reaches a value such that it fires, the capacitor discharges instantaneously almost to zero through it.

The process then starts all over again. A saw-tooth voltage with an amplitude of ca. 200 V is therefore obtained on the condenser. From a potentiometer connected in parallel to the capacitor, a saw-tooth voltage is applied to the voltage amplifier; from its cathode, impulses of the requisite value pass on to the cell.

To improve the linearity of the voltage a tube L_4 with a reverse connection with respect to the current (cathode-grid) is used. In this way the decrease in potential drop across R_1 depends on the change in capacity, i. e. on a decrease in the displacement on the grid of L_1, and consequently the anode current increases with increasing charge on the capacitor. At the moment when the condenser discharges a large displacement occurs on the grid of tube L_1 and the tube shuts off, enabling the condenser to discharge rapidly.

By means of this set-up the potential increase applied to the cell is satisfactorily linear. The effect of the non-linearity of the potential increase on the oscillographic curve is weakened because in such a set-up a saw-tooth wave of exactly the same form is applied directly to the horizontal plates of the oscillograph from the generator. The possibilities of changing the frequency of the impulses applied to the cell up to 50 times/sec was provided for in the generator by including a potentiometer R_1. The generator permits a rate of potential increase of the cell of ca. 100 V/sec. In principle one could get a much higher rate of potential increase and consequently a greater sensitivity. In the actual set-up however the use of a saw-tooth voltage is a limiting factor. The presence of the amplifier L_3 in the first place means a low output resistance for the ganerator so that the effect of the current on the output voltage of the generator is reduced to a minimum, and secondly, permits the amplitude of the saw-tooth voltage applied to the cell to be regulated. In the given set-up the saw-tooth voltage from the amplifier L_3 is applied to the cell with a load resistor. The polarographic cell itself consists of a dropping mercury cathode and a calomel anode assembled separately and screened from electromagnetic fields. A screened resistance box of 100 kΩ serves as load resistor. Its value is changed according to the amplification required (this is determined by the concentration of test element in solution).

The general principles of how to get current-voltage curves are considered at the beginning of this article. Normally the current obtained in a polarographic cell is of the order of a few microamps while the potential drop it gives rise to across a load resistor is of the order of thousands or hundreds of microvolts. It is usually necessary therefore to amplify the voltage $10^4 - 10^5$ times so that the potential drop across the cell can be connected directly to the vertical plates of the oscillograph. A preamplifier is used in conjunction with the oscillograph for vertical amplification. The overall amplification of oscillograph plus preamplifier is sufficient for use with a half-inch tube. In order to eliminate the effect of the next increase in the saw-tooth voltage which begins immediately after the sudden drop of the previous impulse, on the maximum current, a synchronizing system is included so as to synchronize the frequency of the impulses applied to the cell with the drop time.

A mechanical impulse counter based on a non-incandescent thyratron – the MTKh-90, is used in this set-up for determining the rate of voltage change in the cell.

The whole apparatus is supplied from an electronically stabilized source and from accumulators.

Fig. 9. Oscillographic curves of cadmium and zinc on one drop of mercury during its growth: m = 2,6 mg/sec.; t = 3,6 sec.; α = 18 V/sec.

Fig. 10. Oscillographic curve of cadmium and zinc on one drop of mercury at maximal size: m = 2,8 mg/sec.; t = 3,6 sec.; α = 18 V/sec.

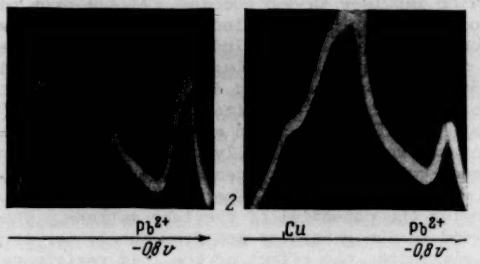

Fig. 21. Determination of lead in the presence of copper and zinc in 0,1 N KNO_3.

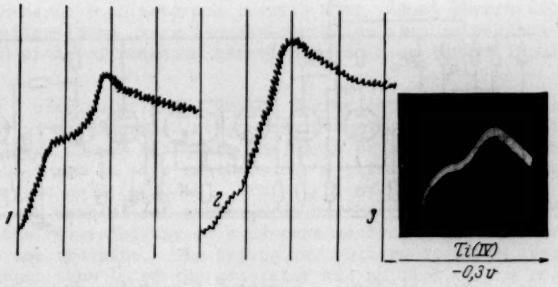

Fig. 22. Polarogramms and oscillogramm in the presence of iron and vanadium.

Figs. 9 and 10 represent oscillographic curves obtained for 10^{-4} M $CdCl_2$ and 10^{-4} M $ZnCl_2$ in 0.1 N KCl, using the oscillographic polarograph of the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry. Electrolysis was carried out using a saw-tooth voltage amplitude of −1.8 V relative to the saturated calomel electrode in the absence of dissolved atmospheric oxygen.

Fig. 9 contains a series of oscillographic curves obtained from one drop of mercury at various stages of its growth, while Fig. 10 was recorded for one drop of mercury at its maximum size during a few fractions of a second before it broke off.

From Fig. 10 it is evident that the oscillographic curves for cadmium and zinc ions appear at potentials of −1.12 and −0.6 V relative to the saturated calomel electrode. One of the most recent constructions described for an oscillographic polarograph which operates on the same principle (saw-tooth voltage) is that of Snowden and Page [8]. These authors give a detailed description of all the component circuits involved. It is built on the same principle as Randles' instrument but it also contains some original refinements; it consists of a generator, a compensator, a synchronizer (delay gate) and an amplifier with a cathode-ray tube. A clipped saw-tooth voltage is applied to the cell. The interval between impulses is 3-6 seconds. At the drop point the voltage impulse from a load resistor R is applied to a synchronizer which is an ordinary vibrator, one anode of which includes a relay with a key K (Fig. 11). The synchronizer is not shown in the diagram. When this is done the uni-vibrator is reversed and the relay is opened during the time the impulse is applied. After the uni-vibrator is returned to its original position (i.e. after 3-6 seconds) the relay is switched on again and the generator started. The generator is a condenser C which periodically charges through a variable resistance from the anode voltage. The apices of the saw-tooth voltage are clipped with a thyratron working as a diode. The amplitude of the clipped saw-tooth is regulated by changing the potential of the tube cathode. The impulse from the generator is applied to the generator and from the latter to the cell. The compensator thereby eliminates the effect of the load resistance on the current flowing through the cell. The change in potential drop across the load resistor is amplified by means of a current amplifier and is applied to the vertical plates of the oscillograph. The horizontal sweep is effected from the same saw-tooth generator. I − E curves are traced on the screen. Snowden and Page's polarograph is a more complex and more refined instrument than preceding ones and extends the boundaries of polarographic analysis.

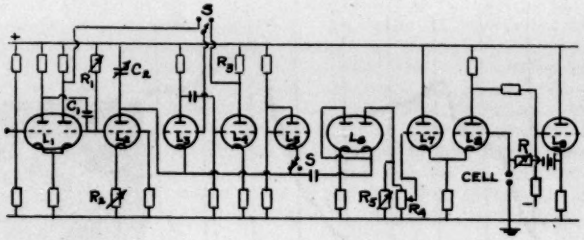

Fig. 12. Cruse and Heberle's Polarograph

Bearing in mind the drawbacks of methods involving saw-tooth voltages noted above, and those of impulse methods which complicate visual observation

for large drop times, Cruse and Heberle [9], used a more universal system than previous authors for their oscillographic studies.

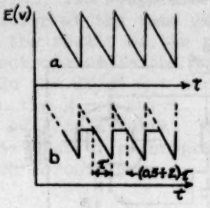

Fig. 13. Saw-tooth voltage (a), converted into impulses (b).

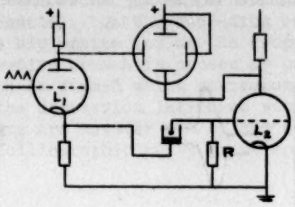

Fig. 14. Seveik's Set-up.

In Cruse and Heberle's polarograph either a saw-tooth voltage or impulses of a linearly increasing voltage with a given delay time can be applied to the polarographic cell. A simplified schematic diagram of their instrument is shown in Fig. 12.

Condenser C_2 is linearly charged through a pentode L_2 to the value of the potential drop across the resistor R_3 and is rapidly discharged on reversing the multivibrator which consists of L_2 and L_4, the cycle is then repeated. A saw-tooth voltage (Fig. 13 a) is thus obtained which is clipped by a diode L_6 and converted into impulses (Fig. 13, b), following each other at intervals 0.5 – 2 times the duration of the impulse itself. Their frequency is determined by the parameters R_2 and C_2, the amplitude by the position of the potentiometer R_4 and the interval between them by the value of R_5. When operating under impulse conditions the switch S is used for switching off the multivibrator L_3L_4 and switching on the univibrator L_1 and L_3. The univibrator is started by an impulse from the vertical amplifier at the moment of drop fall. Under these conditions the delay time of the impulse applied to the cell after drop fall is determined by the value of the circuit R_1C_1 and changes with changes in R_1. The diode switch L_5 is used for restricting the delayed impulses.

The impulses from the generator are applied to the cell through a compensator designed for eliminating the effect of the load resistor R on the current flowing through the cell.

Cruse and Heberle's polarograph permits both visual observation and qualitative determination (when using the saw-tooth voltage) as well as quantitative measurements and study of reaction kinetics to be made (under impulse conditions).

Seveik [10], used an original set-up for an oscillographic polarograph based on the use of a triangular sweep for investigating polarization phenomena. Getting I – E curves was again the basis of his method as in previous work. The new features in this case are the application of triangular impulses to the polarographic cell (Fig. 14). This type of voltage permits one to obtain simultaneously both cathode and anode waves on the polarogram and to make deductions as to the reversibility of a process according to their arrangement with respect to the ordinate. The triangular voltage is taken from the cathode of the output tube L_1 of the generator and applied to the polarographic cell fitted with a load resistor R. The potential drop across the load resistor is amplified by the current amplifier (represented by only one tube L_2) and applied to the vertical plates of the oscillograph. The horizontal sweep is also effected by means of the same triangular voltage taken from the

anode of the output valve L_1 of the generator. Thus on applying to the plates, which deflect the ray horizontally, a triangular voltage, there results a regular movement of the ray along the horizontal on both sides of it.

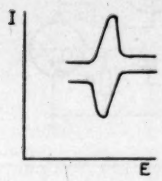

Fig. 15. Oscillogram for Lead taken at ν = 20.8 cycles /sec.

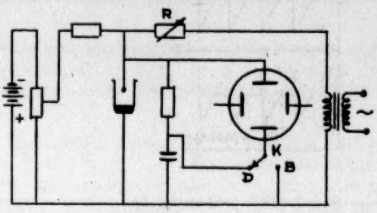

Fig. 16. The Heyrovsky Polarograph. (Schematic)

During the period of growth of the triangular voltage the ray moves from left to right and registers reduction processes (as in the previous set-ups); during the period when the triangular voltage is decreasing the ray moves in the opposite direction and registers oxidation processes. The amplitude of the triangular voltage on the cell was 2 V, frequency (1 – 100) cycles/sec.. Photographs were taken at the last moment of drop growth when the rate of increase of drop surface is very small and the polarographic current does not change.

Fig. 15 represents an oscillogram obtained for 10^{-4} M $Pb(NO_3)_2$ in 1 N NaOH, using Seveik's polarograph. From this graph it can be seen that the maximum current for the upper cathode wave which is caused by reduction of $HPbO_2$ on the dropping mercury electrode and the lower anode wave both appear at practically the same potential, thus testifying to the reversibility of these two electrode processes.

All the types of oscillographic polarographs considered above, independently of the concentration of test material in solution and the character of the investigation, in the final count boil down to recording of I – E curves. In this sense they represent one side of the development of oscillographic polarography along the lines of increasing the limits at which ions can be detected and determined in solution. Seveik's polarograph in addition permits determination of the reversibility of electrode reactions, two curves of I – E (cathode and anode waves) being obtained. There are some characteristic differences in the character of the oscillograms obtained by means of one of the earlier forms of polarographs used by Heyrovsky for establishing the reversibility and rate of electrode reactions [11].

Heyrovsky's polarograph (Fig. 16) gives oscillographic curves of potential against time (E – t) and of dE/dt – t. To do this a direct voltage from a battery and an alternating voltage from a transformer is applied to the cell, the alternating voltage is either of a sinusoidal form with a frequency of 50 cycles per second or in the form of square impulses from a generator. The value of the direct and alternating voltages is regulated potentiometrically. To establish the reversibility and the rate of electrode reactions a switch over to two positions can be effected by means of contact K (Fig. 16). Position KB gives E – t curves on the screen, while in position KD, dE/dt – t curves are obtained.

Fig. 17 represents a potential – time curve and its derivative, which were obtained on a Heyrovksy polarograph for a solution of 1 N NAOH containing $2 \cdot 10^{-3}$ N $Pb(NO_3)_2$. Two steps are visible on both the ascending and descending branches of the curve at the same values of the potential. On the ascending branch, the step is the result of the reduction of the biplumbite ion on the dropping mercury electrode, while the step on the descending branch is caused by oxidation of lead. On the dE/dt – t curve, a depression is formed which corresponds to the steps on the E – t curve. The height of the depression increases with concentration of depolarizers. Exact measurements are however out of the question with this type of polarograph, since the oscillographic curve grows and subsides with each mercury drop.

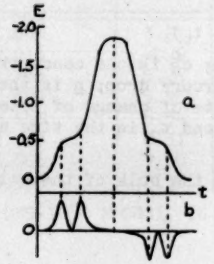

Fig. 17. An (E – t) curve (a), and the derivative curve (b).

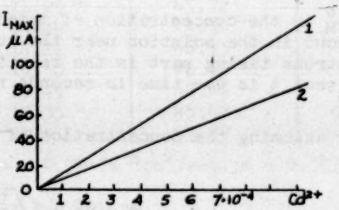

Fig. 18. Values of the Maximum Current for Various Cadmium Concentrations. 1 – Impulse method: 2 – saw-tooth method; Cd^{2+} in 0.1 M KCl; α = 12.5 V/sec; m = 0.835 mg/sec; t = 8.44 sec.

Details of this set-up of Heyrovsky's were published immediately after those of Matheson and Nichol's work, and despite the simplicity of its construction and operating principles it has considerably widened the scope of oscillographic polarography for analytical purposes. This set-up, however, had one serious defect – the difficulty of working out the results because of the non-linearity of potential increase with time.

II. Theoretical Equations.

A. The diffusion current on oscillographic curves.

1). Equations suggested. Fig. 1 represents an oscillographic curve for cadmium on which the section AB corresponds to the maximum capacity current while the part CDE corresponds to the diffusion current of Cd, and CD the maximal diffusion current. It has been established that there is a linear relation between maximum current and concentration of material in solution.

As in ordinary polarography, in deriving an equation for the limiting diffusion current, considerable attention has been paid in oscillographic polarography to deriving an equation for the maximum current (point D on the section CD of Fig. 1). It is only very recently that a new modification of the semi-empirical Ilkovich equation for the limiting diffusion current in ordinary polarography was suggested by Stackelberg [12], it is of the following form:

$$I_g = 619ncD^{1/2} g^{2/3} t^{-1/2}(1 + 17D^{1/2} g^{-1/3} t^{1/2}), \qquad (1)$$

where n is the number of electrons participating in a reaction; c is the concentration of material in millimols/ liter; D is the diffusion coefficient of the material in cm^2/sec; t is the drop time of the capillary and $g = mt$ (m is the amount of mercury in mg flowing through the capillary per second.

If all the constants included in the equation are taken into account this modified Ilkovich equation can be changed into an equation which was derived by one of the authors of the present article [13]. Randles [14], and Seveik [10], independently derived equations for the maximum current of the oscillographic curve for the case where the electrode reaction is reversible and the reaction products are soluble in water.

Assuming that the rate of change of electrode potential relative to the solution is constant, Randles showed that

$$\frac{0.059}{n} \log (c_M^o/c_S^o) = \alpha(t - t_o), \qquad (2)$$

where c_M^o is the concentration of metal in the amalgam; c_S^o is the concentration of metal ions in the solution near the surface of the mercury drop; n is the number of electrons taking part in the reaction; α is the rate of change of potential in volts/ sec; t is the time in seconds relative to t_o, and t_o is the time at which $c_M^o = c_S^o$.

By assuming the concentration of the test ion in the bulk of the solution to be

$$c = c_S^o + \sqrt{\frac{D_M^o}{D_S}} \cdot c_M^o \qquad (3)$$

(D_M^o is the diffusion coefficient of metal in the amalgam, D_S is the diffusion coefficient of the ion in solution), and solving the equation for linear diffusion graphically [15], Randles found that

$$I_{max} = \frac{1.24\pi F c}{0.0118^{1/2} \cdot 10^3} n^{3/2} \gamma^{2/3} t_{max}^{2/3} \alpha^{1/2} D^{1/2}, \qquad (4)$$

where I_{max} is the maximum value of the current of the oscillograph wave expressed in amperes; t_{max} is the time in the course of which I_{max} is attained; F is the Faraday number; γ is defined by the relation $r_o^3 = 3mt/4\pi d = \gamma t$, i.e., $\gamma = 3m/4\pi d$ (m is the amount of mercury in g issuing from the capillary/sec., d is the density of mercury, t is the drop time of the capillary, D is the diffusion coefficient of the reduced ion, and c is the ionic concentration expressed in mols/liter. The remaining legends in (4) are the same as in equation (2).

Substituting the numerical values in equation (4) we find that

$$I_{max} = 234.4 n^{3/2} \cdot m^{2/3} \cdot t_{max}^{2/3} \alpha^{1/2} \cdot D^{1/2} \cdot c \text{ amperes} \qquad (5)$$

where all the legends are the same as in equation (4). Using the linear diffusion equation and taking into account the boundary conditions of the electrolysis and introducing hyperbolic functions into a series of equations, Seveik derived the following equation for the maximum current of the oscillographic curve:

$$I_{max} = 0.0191 \cdot F n^{3/2} m^{2/3} t_{max}^{2/3} D^{1/2} \alpha^{1/2} c \text{ microamperes}$$

where m is expressed in mg/sec, while c is the concentration in millimols/ liter. The remaining legends are same as in equations (2) and (4).

It is not difficult to see that equations (2) and (4) are identical apart from the constant. The modified Ilkovich equation [Equation (1)] is externally similar to the equations of Randles and Seveik.

TABLE 1

Effect of Rate of Change of Potential on the Maximum Current of Cadmium

$1.039 \cdot 10^{-4}$ M $CdCl_2$ in 0.1 N KCl; $D_{Cd^{2+}} = 0.52 \cdot 10^{-5}$ cm²/sec; m = 0.835 mg/sec; t_{max} = 8.44 sec; h = 270 mm; experimental temperature 25° ± 0.1°.

$\alpha^{1/2}$, where α- is the rate of change of potential in V/sec.	Maximum Current of Reduced Ion			Difference in % between experimental values and those calculated by means of Seveik's equation	Difference in % between experimental values and those calculated by means of Randles' equation
	Found, in μA	Calculated from Seveik's equation, in μA	Calculated from Randles' equation, in μA		
1.686	3.97	7.39	9.39	46.27	60.62
2.016	4.79	8.83	11.23	45.72	57.31
2.363	5.73	10.33	13.14	44.50	56.37
2.509	5.95	11.47	14.21	46.73	58.13
2.649	6.54	12.03	15.30	45.60	57.23
2.795	6.51	12.14	15.44	46.42	57.89
3.006	7.50	13.65	17.35	45.07	56.79
3.536	8.38	16.05	20.41	47.79	58.95
$1.039 \cdot 10^{-4}$ M $CdCl_2$ in 0.1 N KCl; $D_{Cd^{2+}} = 0.52 \cdot 10^{-5}$ cm²/sec.; m = 0.347 mg/sec.; t_{max} = 14.5 sec.; h = 270 mm					
1.820	3.75	6.45	8.21	41.84	54.34
2.492	6.17	8.83	11.24	30.07	45.07
2.547	6.39	9.24	11.75	30.77	45.58
2.882	7.72	10.44	13.29	26.21	41.92
3.077	9.48	11.16	13.88	15.03	31.69
3.544	11.02	12.85	15.99	14.20	31.06
3.625	11.03	12.86	16.36	14.23	32.58
3.751	11.69	13.60	16.93	14.05	30.96
4.156	12.57	14.72	18.75	14.60	32.95

2) Checking the Theoretical Equations of Randles and Seveik.

Randles [14], and Sevčik [10], investigated the effect of the rate of potential change on the value of the maximum current of the reduced ion. The ratios of $I_{max}/\alpha^{1/2}$ were found to be approximately equal to the theoretical values.

Delahay [16], also studied the relation between maximum current and the square root of the rate of change of potential for cadmium, zinc, and nickel ions. Delahay plotted the values of I_{max} found, on the ordinate and corresponding values of $\alpha^{1/2}$ on the abscissa. The curves for cadmium are practically straight lines. For three concentrations of zinc(1; 0.5; 0.2 mM) it was found that at low rates of potential change the results relating I_{max} with $\alpha^{1/2}$ deviated only slightly from linearity, but at high values of the rate of potential change there was considerable deviation from linearity.

The maximum value of the current for 1, 0.5, and 0.2 mM of zinc calculated from equation (5) for $\alpha^{1/2} = 5.75$ were found to be 258, 129, and 54 μA, respectively, while the corresponding experimental values for the same zinc concentrations were 56, 37, and 11 μA.

The percentage deviations between theory and experiment were 78, 71, and 80, respectively, which are considerably in excess of the 28% deviation of the theoretical values from the maximum current found by Randles at $\alpha^{1/2}$=0.51 V/sec.

In order to check on the equations of Randles and Seveik in more detail we carried out a number of tests on the study of the effect of the rate of change of potential on the maximum current of cadmium. 0.1 N KCl containing $1.039 \cdot 10^{-4}$ M $CdCl_2$ was electrolyzed in the absence of atmospheric oxygen for different rates of potential change. Electrolysis was carried out using two dropping mercury electrodes of differing drop time.

The mean values of the actual diffusion coefficient of Cd^{2+} determined by a diffraction method [17], were substituted in the equations of Randles and Seveik, respectively. The rate of change of potential applied to the cell depends on the frequency of the sweep generator (ν) and on the amplitude of the saw-tooth voltage ($E_\sim$). The product of these two factors gives the rate of change of the saw-tooth voltage (α) applied to the cell.

Experimental and calculated results are included in Table 1. The values of the maximum current correspond to the last instant of drop growth when the rate at which the surface of the drop increases becomes very small and the polarographic current hardly changes. For comparison, calculated values are taken as 100%. The calculated values of the maximum current for Cd adduced in Table 1 correspond to the case where the next increase in potential starts immediately after the sudden drop of the previous impulse. We call this method of applying the potential to the cell electrodes the saw-tooth method in contrast to the impulse method in which the impulse is applied to the electrolytic cell with some delay after the beginning of drop formation.

The results given in Table 1 show that the values of I_{max} calculated according to Randles' equation deviate to a considerably greater extent from the experimental values of the cadmium maximum current than those calculated according to Seveik's formula. The slower the drop rate the smaller the deviation between calculated and observed results. With increasing rate of potential change for a very slow drop time (14.5 sec.) the percentage deviation between the experimental results and those calculated by Seveik's equation rises to 14, while on further increasing α the deviation becomes practically constant. The values of the cadmium maximum current calculated according to Randles' equation differ from the $I_{max.}$ values calculated according to Seveik's equation by approximately 12 – 18%. This deviation between the values of I_{max} calculated by means of equations (5) and (6) can be explained by the fact that Randles solved the linear diffusion equation less accurately than Seveik. Moreover in deriving his equation for the maximum current Randles assumed that the concentration of test ion in solution is equal to its concentration near the mercury drop surface plus the product of the concentration of metal in the amalgam and the square root of the ratio of the diffusion coefficient of the metal in the amalgam to the diffusion coefficient of the ion in solution. These assumptions however are innaccurate, since diffusion conditions toward the dropping mercury electrode differ from the conditions assumed by Randles.

The passage of a current through an electrolytic cell can be regarded as a special case of a heterogeneous chemical transformation [18]. Like all heterogeneous transformations it consists of three stages: a) transfer of ions from the depth of the solution to the electrode surface, b) a particular electrochemical reaction (discharge of ions on the cathode or their formation on the anode), c) formation of reaction end products and their precipitation on the electrode surface. The system mercury electrode-metal ions represents a system in which the discharge products are removed in the case where the metal forms an amalgam with mercury. The discharged metal ions in the form of atoms dissolve in mercury [e. g. $Cd^{2+} + 2\ e + Hg \rightleftharpoons Cd(Hg)$] and are removed from the surface by agitation. The boundary, metal-solution, in the case considered is a membrane which is permeable to discharged particles.

In oscillographic polarography where the rate of potential increase applied

to the cell differs somewhat from the rates used in ordinary polarography, the transfer of ions from a solution containing enough supporting electrolyte to the electrode surface is realized by spherical diffusion which is considerably more rapid than in ordinary polarography. As a result the concentration gradient in the layer near the electrodes is greater than the value of $(dc/dr)_{r=0}$ in the effective diffusion layer obtained as the result of a slow increase in applied potential, i.e. as in the case of ordinary polarography. Thus for an equal concentration of the test ion the value of the maximum current of the reduced ion is considerably greater than the value of the limiting current. On applying a saw-tooth potential to the cell the diffusion rate varies with the time, as can be seen from the oscilograms shown in Figs. 9 and 10.

The electrochemical reaction itself proceeds very rapidly and the slow stage of the process is the diffusion stage. As a result the overall velocity of the electrochemical transformation is determined by the rate of spherical diffusion to the stationary mercury surface which is the slowest stage of the process. In the case of the saw-tooth method however the removal of reaction products from the mercury drop surface is of essential significance. This stage of the process is slow in comparison with the rate at which the saw-tooth voltage is applied, and also shows an effect on the value of the maximum current of the reduced ion. Since under saw-tooth operating conditions the next increase in potential follows on immediately after the sudden drop of the previous impulse, i. e. when the ions reduced on the dropping electrode have not yet succeeded in being completely oxidized and distributed in the layers which are further removed from the electrode surface, then some of the oxidized ions remain near the electrode, as a result of which the concentration gradient in the diffusion layer becomes less than that forecast if only symmetrical spherical diffusion to the stationary electrode for a rapid potential change on the electrode is taken into account. In practice, as a result, the values of the current obtained are low in comparison with the true values of the polarographic current calculated from the diffusion equation.

What has been said is illustrated by the curves adduced in Fig. 18. Concentration of cadmium in mols/liter is plotted along the abscissa while the maximum current for Cd^{2+} is plotted along the ordinate. From the results given in Fig. 18 it follows that in the case of the impulse method the values of I_{max} are considerably greater than those obtained by the saw-tooth method.

Experiments; the results of which are given in Table 1 show that the significant deviation of experimental results from the calculated values is probably a result of the fact that Randles and Seveik in deriving their respective equations for the maximum current used the differential equation for linear diffusion instead of the equation for spherical diffusion, and of the fact that they did not take into account the rate of removal of the reaction products from the surface of the mercury drops when using the saw-tooth method. It follows from the results given in Table 1 that with increasing rate of saw-tooth potential change the maximum current of the reduced ion increases.

On a mercury electrode with a low drop rate the values of the maximum current of the reduced ion are considerably greater than I_{max} obtained on an electrode with short drop time. Compare in Table 1 experiments carried out for practically the same values of $\alpha^{1/2}$, e. g. for 3.006 and 3.077 and for 3.536 and 3.544. The reverse is observed in ordinary polarography. For a slow dropping electrode the values of the limiting current are less than I_{max} obtained when using a capillary with a short dropping period. E. g. for $5.9 \cdot 10^{-3}$ M $CdCl_2$ in 0.1 M KCl using a capillary for which m = 4.6 mg/sec and t = 2.36 sec, it was found that the limiting current is equal to 35.34 μA while in a solution of 0.1 M KCl containing $6.5 \cdot 10^{-3}$ M $CdCl_2$ using a capillary with the characteristics; m = 0.847 g/sec and t = 7.33 sec, $I_{limiting}$ was 28.21 μA.

By solving the equation for non-stationary diffusion to a stationary spherical mercury electrode and taking into account the concentration distribution of reaction products at various distances from the surface of the mercury drop when operating under saw-tooth voltage conditions, we got the following semi-empirical equation for the maximum current of the oscillographic wave:

$$I_{max} = 1034.4n^{3/2}cD^{1/2}m^{2/3}t^{2/3}\alpha^{1/2} - 8425n^3c^2Dm^{4/3} \qquad (7)$$

where m is expressed in mg/sec; c is the concentration in millimols/liter.

TABLE 2

Effect of Rate of Potential Change on the Value of the Maximum Current of Cadmium.

$1.039 \cdot 10^{-4}$ M $CdCl_2$ in 0.1 N KCl; $D_{Cd^{2+}} = 0.52 \cdot 10^{-5}$ cm^2/sec.; m = 0.835 mg/sec.; t_{max} = 8.44 sec.; h = 270 mm; experimental temperature 25.0° ± 0.1°

$\alpha^{1/2}$ where α is the rate of potential change in V/sec.	Maximum current of the reduced ion		Difference in % between calculated and experimental results
	Found in μA	Calculated by means of equation (7) in μA	
1.686	3.97	4.15	−4.37
2.016	4.79	4.93	−2.73
2.363	5.73	5.74	−0.16
2.509	5.95	6.07	−1.98
2.795	6.5	6.72	−3.23
3.006	7.50	7.20	+4.16
3.536	8.38	8.37	+0.09

The remaining legends are the same as in equations (2) and (4). The maximum current is expressed in microamperes.

Using equation (17) we calculated the maximum current for cadmium and compared the results obtained with experimental results. Both calculated and experimental results are given in Table 2. Calculated values are taken as 100%.

Table 2 shows that experimental and theoretical results are in good agreement.

The respective equations of Randles and Seveik were derived for reversible electrode processes. For irreversible processes, Delahay [19], proposed the following equation for the maximum current of the oscillographic wave.

$$I_{max} = 2.56 \cdot 10^5 n(an_a)^{1/2}m^{2/3}t^{2/3}D^{1/2}c\alpha^{1/2} \text{ amperes} \qquad (8)$$

where a is a coefficient characteristic of the degree of irreversibility of the electrode process; n_a – the number of electrons participating in the reaction which determines the reaction velocity; c – the concentration in mols/cm^3; m – the amount of mercury in g issuing from the capillary/sec. The remaining legends are the same as in equations (2) and (4).

Equation (8) has not been checked experimentally.

B. The Capacity Current on Oscillographic Curves

The existence of a current independent of whether or not electrode processes occur on the electrode surface is related to drop growth and to the presence of a double electrical layer on the boundary between drop and solution. Drop growth at a constant potential, independently of any electrochemical reactions, is accompanied by a current which is called the charging current. When the applied

voltage is less than 0.5 V relative to the normal calomel electrode, the current which passes is negative, i. e. it is in the reverse direction to that of the reduction current. At higher potentials it changes its sign.

In oscillographic polarography, as the result of a rapid increase in the potential applied to the cell and the shape of the impulse applied to the dropping electrode, the capacitor current is considerably greater than the charging current obtained in ordinary polarography.

When a saw-tooth voltage is applied to the cell, it is reckoned [20] and [21], that the capacitor current may be expressed by the following equation:

$$i_c = 0.00846\ m^{2/3}t^{2/3}cdE/dt \text{ microamperes} \qquad (9)$$

where m – is the amount of mercury issuing from the capillary/sec; c – the capacity of the double layer in micro-farads (μF)/cm^2, t – the dropping time of the capillary, dE/dt – the rate of change of potential.

Delahay and Stiehl [22], suggested the formula given below, which differs somewhat from equation (9):

$$i_c = 4.81(m/d)^{2/3}t^{2/3}\left[E\frac{dc}{dE} + c\right]\frac{dE}{dt} + 3.20c(m/d)^{2/3}t^{-1/3}E, \qquad (10)$$

where E – is the value of the saw-tooth voltage applied to the cell; and d – the density of mercury. The other legends are the same as in equation (9).

The capacitor current must be considered at a definite value of the maximum current. Distortion of the oscillographic wave can be considerable when I_{max} is less than the charging current. Usually the value of the maximum current is determined graphically as shown in Fig. 19. In curve A the charging current initially increases rapidly and becomes constant at the reduction or oxidation potential of the ion. By producing the line for the capacitor current paralled to the abscissa the value of the maximum current can be determined.

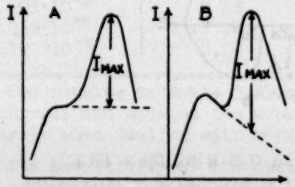

Fig. 19. Measuring the value of the maximum current without taking into account the capacitor current.

When the oscillographic curve has the shape shown in Fig. 19 B, the line is produced as shown in Fig. 19 and I_{max} calculated. When concentrations of less that 10^{-3} mol/liter are dealt with, it is necessary to establish by means of a separate experiment the capacitor current from an oscillogram for a solution of the supporting electrolyte at the same potential at which the maximum current is measured. The value of the charging current thus obtained is subtracted from the value of I_{max}.

III: Qualitative Analysis.

Heyrovsky [11,23], was one of the first to use an oscillographic method for qualitative analysis. The voltage-time curves and their derivatives obtained by means of an oscillographic polarograph (Fig. 17) permit one to detect various ions in solution from their half-wave potentials or from their oscillographic spectra. If one or more steps are formed on the voltage-time curve, then by using a high frequency generator it is possible to draw out the steps so that they assume the form of spectral lines. Fig. 20 illus-

trates the spectral lines obtained for a solution of 0.5 N NH_4OH + NH_4Cl containing $HgSO_3^-$, Tl^+, Cd^{2+}, Zn^{2+}, Fe^{2+}, Mn^{2+}. The positions of these lines on the ordinate scale, i. e., their potentials, correspond to the usual half-wave potentials obtained when using ordinary polarography. By comparing this empirical scale of deposition potentials with the potentials of the edge lines of the spectra, which depend on the composition of the supporting electrolyte, it is possible to carry out qualitative determinations.

If there are no means available for registering the spectra, then it is still possible to carry out qualitative determinations by establishing the positions of peaks on the voltage-time curve. In this way it is possible to detect inorganic and organic depolarizers in concentrations from 10^{-4}N.

Heyrovsky [24], also developed a method of getting dE/dt – E curves. Such curves in certain instances give more information than an ordinary polarogram, since the effect of anode polarization which does not appear on current-voltage curves, i. e., in ordinary polarography, can in addition identify the depolarizer [11]. Indium which cannot be determined polarographically in the presence of cadmium is recorded on the anode branch of the dE/dT – E curve, as can be seen from the diagram adduced in Fig. 20 B. This diagram was recorded for a zinc ore containing traces of lead, cadmium, and indium. The dE/dt – E curves are particularly valuable for the analysis of mixtures of organic isomers. In such a case when a dropping mercury electrode is used, very complex curves are obtained because of side reactions. On the other hand, a streaming electrode [25] is polarized to give a simple picture with minima at characteristic potentials whereby it is possible to distinguish [26, 27] ortho-, meta-, and para-nitrophenols in the presence of nitrobenzene. Similarly the isomers: nicotinic, picolinic, and isonicotinic acids can be distinguished in 2 N sulfuric acid.

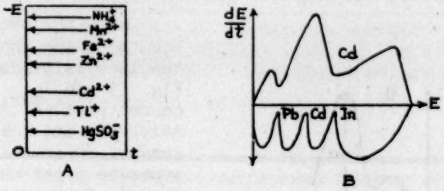

Fig. 20 A – Scale of the spectrum in 0.5 N NH_4OH + NH_4Cl; B – the curve dE/dt – E for 2 N sodium hydroxide – potassium cyanide. Upper curve, cathode process; lower curve, anode process.

Atmospheric oxygen only affects derivative curves in acid media and even here does not interfere with this type of analysis too much.

When a dropping electrode is used for oscillographic studies it is sufficient to use only a few mls of solution in a small, open beaker.

When a streaming electrode is used, 15 – 18 ml of solution is required. Qualitative measurements of half-wave potentials obtained by oscillographic methods by Miller [28], and Boeke and Suchtelen [29], are comparable in accuracy with ordinary polarography. E.g., Miller got a half-wave potential for cadmium of -0.627 - 0.629 V relative to the saturated calomel electrode, which is in good agreement with the result of ordinary polarography.

Snowden and Page [8] differentiated the I – E curve to get "breaks" on the oscillographic curve at points near to the maximum current. The potentials at which these breaks were obtained gave an indication of the qualitative composition of the test solution.

The GEOKhI oscillographic polarograph [7], which operates on a saw-tooth voltage permits evaluation of the qualitative composition of a solution from the potentials corresponding to peaks on the I – E curves.

IV. Quantitative Analysis.

According to equations (5), (6), (7), and (8) the values of the maximum diffusion current are proportional to the concentration of test material in solution when saw-tooth or impulse methods are employed. It has been shown experimentally [4,5,7,10], that the linear relation between I_{max} and concentration of test material in solution both for reversible and irreversible processes only holds for a constant rate of potential change and for equal pressures on the dropping mercury.

As illustrations, we have adduced in Tables 3, 4, and 5 results obtained using the GEOKhI polarograph in the absence of atmospheric oxygen.

TABLE 3

Maximum value of the current for various concentrations of cadmium in 0.1 N KCl;

h = 270 mm; m = 0.347 mg/sec.; t = 14.5 sec.; α = 17.27 V/sec.

Concentration of cadmium, in mol/liter	Maximum value of current, in μA
$1.039 \cdot 10^{-4}$	12.57
$5.195 \cdot 10^{-5}$	6.32
$1.039 \cdot 10^{-5}$	1.28
$5.195 \cdot 10^{-6}$	0.68
$1.039 \cdot 10^{-6}$	0.14
$5.195 \cdot 10^{-7}$	0.08

TABLE 4

Maximum values of the current for various concentrations of lead in the presence of copper and zinc in 0.1 N KNO_3

m = 0.352 mg/sec.; t = 11.3 sec; α = 11.16 V/sec.

Concentration of lead, in μg/ml	Maximum value of the current, in μA
20.8	6.93
10.4	3.42
5.2	1.70
2.08	0.81
1.04	0.43
	–

The results in Table 3 show that there is a linear relation between maximum current and cadmium ion concentration; there is a slight deviation from linearity when dealing with very dilute solutions.

The sensitivity of the oscillographic method is considerably higher than that of ordinary polarography, the latter can only determine 10^{-5} M $CdCl_2$ when a multi-capillary mercury electrode is used [30]. At concentrations less than 10^{-5} mol/liter we could not get a definite cadmium wave on the voltage-ampere curve obtained with an ordinary Heyrovsky polarograph because it fused into the supplementary current wave [37].

The results given in Table 4 show that the linear relation between lead concentration and the maximum current for lead is maintained in the presence of accompanying ions. Two oscillograms are given in Fig. 21 for potassium nitrate containing copper, lead, and zinc. E = –0.9 V was chosen in this case for lead determination. The oscillograms were recorded for one drop of mercury at its maximum cross-section corresponding to the moment at which the drop is about to fall off, at a rate of potential change of 9.8 V/sec.. The oscillograms, which are really voltage-ampere curves, show from the left a sharp rise on the curve caused by the discharge current of the mercury sur-

face and the shape of the applied impulse and by the reduction of the copper. This is followed by a sudden drop until lead is reduced on the dropping mercury cathode; this occurs at an amplitude value of the saw-tooth voltage of − 0.8 V relative to the anode mercury. The lead waves are clearly defined and can be measured exactly.

The lead waves on Curves 1 and 2 correspond respectively to 20 and 10 μg/ml. The values of the maximum current of lead are respectively 5.23 and 2.62 μA, which indicate a strict linearity between concentration and $I_{max.}$.

Cadmium and lead ions are reduced reversibly on the dropping mercury electrode, while Zn^{2+} is irreversibly reduced (re reversible and irreversible processes, see below).

In order to check whether or not there is a linear relation between the concentration of the reduced ions and the value of its maximum current for irreversible processes, a number of experiments were carried out on the electrolysis of Zn^{2+} solution.

Table 5 contains results of the maximum current of zinc in 0.1 N KNO_3 in the presence of lead and copper ions.

TABLE 5

Maximum values of the current for various concentrations of zinc in the presence of lead and copper in 0.1 N KNO_3; m = 0.347 mg/sec.; t = 12.5 sec.; α = 18.6 V/sec.

Zinc concentration in μg/ml	Maximum values of the current in μA
9.90	11.91
4.90	6.03
1.88	2.41
0.94	1.24
0.47	0.64

These results show that a linear relation exists between concentration of zinc ions in solution and the maximum current of zinc. At very high dilutions there is some deviation from linearity. Experiments on zinc determinations showed that the sensitivity of the oscillographic method can be increased up to 10^{-6}%.

By means of the oscillographic polarograph it is possible to determine titanium quantitatively in the presence of considerable amounts of iron and vanadium without preliminary separation of the latter; this is however impossible to carry out by ordinary polarography in which the Fe (III) and V (V) have to be separated beforehand from the titanium [31].

What has been said is illustrated by the curve adduced in Fig 21. These curves were obtained in 1 N H_2SO_4 saturated with sodium oxalate; 1 ml of the respective solutions contained:

10 μg Ti(IV) + 40 μg Fe(III); 10 μg Ti(IV) + 40 μg V(V);
10 μg Ti(IV) + 75 μg V(V) + 500 μg Fe(III).

The first and second curves were obtained with an ordinary polarograph. For an iron content 4 times greater than that of titanium the polarogram of the latter is distorted and a maximum is obtained on the E − I curve (Curve 1, Fig. 22).

When the concentration of vanadium is four times that of titanium, a maxi-

mum appears on the curve and the limiting current decreases with increasing applied potential. The origin of the curve is not clearly defined either (Curve 2, Fig. 22). Curve 3 represents an oscillographic photograph of the process occurring on a mercury drop of maximum size. A titanium wave is clearly defined on the E – I curve, this appears at an amplitude of the saw-tooth voltage of –0.30 V relative to the saturated calomel electrode.

It was established that if the amount of iron and vanadium were 100 and 20 times respectively that of Ti (IV), then they have practically no effect on the value of I_{max} for titanium. On a basis of the study of the effect of accompanying elements we succeeded in working out a rapid method for the determination of titanium in steels without preliminary separation of vanadium and iron [31].

V. A Study of the Reversibility of Electrode Reactions.

Any electro-chemical reaction can be considered either as reducing, when the reactants acquire electrons (on the cathode) or as oxidizing when they donate electrons (to the anode). Oxidation-reduction reactions are usually divided into reversible and irreversible reactions.

A reversible reaction is one which satisfies the following conditions:

a) When an inert electrode is immersed in the test solution a definite potential is established on the electrode, which depends only on the concentration and nature of the oxidized and reduced reaction products. Its potential should be independent of the material and the state of the surface of the electrode.

b) On passing a current of sufficiently low density through the electrode its potential should be hardly displaced at all from its equilibrium value, and should not take into account concentration polarization.

Oxidation-reduction reactions which do not satisfy these conditions are called irreversible. Each time there is an electrochemical reaction with a measurable velocity, i. e., every time current passes through the electrode, this leads to some break-down in the thermodynamic equilibrium, and thus leads to a shift in the electrode potential from its equilibrium value.

In the case of the dropping mercury electrode the half-wave potential ($E^{1/2}$) of a simple metal ion depends on the equilibrium potential of the metal, its solubility in mercury and its affinity for mercury [32]. Theoretical values of $E^{1/2}$ have been worked out for some ions and have been compared with experimental values [33]. It was found that the half-wave potentials of lead and zinc do not differ appreciably from the ordinary normal potentials of these metals; this indicates the reversibility of these electrode processes.

Oscillographic polarography has shown however that Zn^{2+} is reduced irreversibly on the dropping mercury electrode, since the cathode and anode processes occur at different potentials. This example shows that it is better to study reversibility and irreversibility of electrode processes by means of oscillographic polarography than by ordinary polarography (from the value of the slope of the straight line obtained by graphical analysis of the equation for the polarographic wave) [33].

In polarography a reversible electrode process is that process for which both cathode and anode processes occur at the same potential while the rates of the two processes are so fast that the durrent is determined only by diffusion.

Heyrovsky [11, 34], used the term " oscillographic irreversibility" for emphasizing the differences between anode and cathode processes. At present some authors prefer to consider the question of irreversibility from three view-points.

1) Anode and cathode processes occur rapidly enough at various half-wave potentials. This implies a different mechanism for the two processes.

2) Anode and cathode processes occur at the same potentials, but the rates of the reduction or the oxidation processes, or of the two together, are low, diffusion is not of great significance, and the limiting current is determined only by the kinetics of the electrode reaction.

3) The third view point is a combination of both the other two. The first two are the view-points most often met in the literature.

The irreversibility of an electrode process in oscillographic polarography is manifested on the curves in various forms. E.g., if a saw-tooth voltage is applied to the cell and the process is irreversible then the peak on the oscillographic curve I - E will be more obtuse than if the process is reversible. If an irreversible process is observed during electrolysis, then on using a triangular sweep, $E^{1}/_{2}$ will not coincide on the cathode and anode branches of the I - E curve. From the extent of the deviation of the half-wave potentials of the oxidation and reduction processes it is possible to judge the degree of irreversibility [10] (see Fig.15). If the electrode process is reversible then on the potential - time curves obtained by means of a Heyrovsky oscillographic polarograph, a symmetrical arrangement of steps will be obtained on the ascending and descending branches of the curve (see Fig.17). When this technique is used and an irreversible process occurs on the electrode, steps are again observed on the cathode and anode branches of the curve but not at the same potential. The degree of irreversibility of an electrode process can also be established from the deviation of the value of the maximum current (on the I - E curve) from the value of I_{max}, calculated by means of equation (7), for various values of potential change (see Table 2). Finally it is possible to determine the degree of irreversibility of an electrode process from the relation between maximum current and mercury pressure. For reversible systems, the maximum current is, theoretically, independent of mercury pressure [see equations (5), (6), and (7)].

1. I - E Curves.

a). The shape of the peak on the I - E Curve. Randles [14] investigated the reduction of several ions on a dropping mercury electrode in order to study the reversibility and irreversibility of electrode processes; he established that reversible reactions under saw-tooth operating conditions are characterized by an acute peak, as in the case of the reduction of Cd^{2+} in 1 N KCl (Fig.23, A). For reactions which deviate from reversibility more obtuse peaks are obtained on the I - E curve, as in the reduction of zinc in 1 N KCl (Fig.23, B). Nickel and cobalt give even more obtuse peaks on the I - E curve than Zn^{2+}, since the degree of irreversibility is more marked in Ni^{2+} and Co^{2+} than in Zn^{2+}. The shape of the peak also depends on the number of electrons participating in the electronic reactions. For Bi^{3+} the peak is more acute than for Cd^{2+}, while the latter has a more acute peak than thallium.

b). The Value of the Maximum Current. According to equations (5), (6), and (7), the value of the maximum current should depend on the rate of change of saw-tooth potential applied to the cell (α).

Delahay [16], studied the effect of $\alpha^{1/2}$ on the value of the maximum current of the reduced ion and compared the experimental results with values calculated by means of Randles' and Seveik's equations. He got an insignificant deviation between the values of I_{max} for Tl^{+} calculated by Randles' equation and the experimental values. For Pb^{2+} and Cd^{2+}

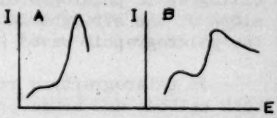

Fig. 23. Shape of the oscillographic curves for saw-tooth sweeps.
A - for the reduction of Cd^{2+} in 1 N KCl; B - for the reduction of Zn^{2+} in 1 N KCl.

however, the deviations were considerable. Significantly greater deviations between the theoretical and experimental values of the maximum current were found for Ni^{2+} and the iodate ion, which are reduced irreversibly on the dropping mercury electrode. These considerable deviations between theory and experiment cannot, however, be attributed entirely to the characteristics of the electrode reactions, since cadmium and lead are reduced reversibly on the mercury electrode. These deviations are predominantly caused by the mechanism of electrolysis during the rapid increase of the saw-tooth voltage on the cell [35,36]. Since equations (5) and (6) do not take into account the characteristics of electrolysis during saw-tooth voltage operating conditions, they cannot serve as criteria for explaining the degree of irreversibility of an electrode process (ee the results given in Table 1).

The electrolysis conditions which hold for saw-tooth operating conditions were taken into account in deriving equation (7), so that it is possible to use the equations for studying the degree of irreversibility of an electrode process (see the results given in Table 2).

According to equations (5) and (6) the value of the maximum current is proportional to the product $m^{2/3} \cdot t^{1/3}$, i.e. to the drop surface. Since the latter is independent of the pressure of the mercury column, it can be deduced that, if all the other factors included in equations (5) and (6) are constant, then I_{max} does not depend on the height of the mercury column [6]. As examples we have adduced a number of curves in Fig.24 which relate maximum current to the height of the mercury column. The height of the mercury column is plotted along the abscissa, while the percentage deviation from the value of the maximum current obtained for a mercury column of height 15 cm is plotted along the ordinate (the value of I_{max} at a mercury column height of 15 cm is arbitrarily taken as 100%).

Fig.24 shows that the value of the maximum current does depend to some extent on the height of the mercury column. Insignificant deviations from a straight line are observed for Cd^{2+}, and Pb^{2+}; greater deviations are obtained for Zn^{2+} because Zn is irreversibly reduced on the dropping mercury electrode.

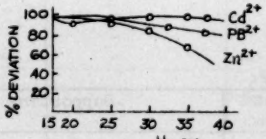

Fig.24. Relation between maximum current and height of mercury column.

c) I - E Curves obtained by means of Triangular Voltage Impulses.

I - E curves obtained by means of Seveik's set-up [10] have the advantage of giving a complete picture of the electrode process, showing cathode and anode processes. A typical I - E curve is shown in Fig.15. Seveik [10] points out that in order to find the half-wave potential on the cathode branch of the curve it is necessary to add $40/n$ mV[1] to the value found for the potential at which the current has its maximum value, where n is the number of electrons participating in the electrode reaction. To determine $E_{1/2}$ on the anode branch of the curve, the same factor has to be subtracted from the value of the potential at which I_{max} is obtained. If the potentials of the two half-waves are the same, then the electrode process can be regarded as reversible. An I - E curve obtained for a reversible process is shown in Fig.15

During the electrolysis of a solution of 1 N NH_4Cl and 1 N NH_4OH, containing zinc, Seveik found that the value of $E_{1/2}$ on the cathode branch differed from that on the anode branch by 0.22 V. This difference between the two half-wave potentials on the respective curves shows that in ammoniacal solutions zinc is reduced irreversibly. The I - E curve obtained for zinc in ammoniacal solution is shown in Fig. 25 A. If to 1 N HCl containing Cd^{2+} there is added freshly prepared gelatin solutions, so that its concentration is 0.005%, then the I - E

1) See Seveik's articles [10], Equations 1, 24.

curves shown in Fig. 25 B which are of a different shape are obtained. No peaks are obtained on the cathode and anode branches of the curve. A small increase in current is observed on both branches of the I - E curve. Fig.25 B shows that even insignificant amounts of freshly prepared gelatin added to the test solution leads to a hindering of the electrochemical processes.

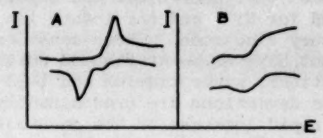

Fig.25. Voltage-current curve (I - E) for irreversible processes.

A - Zn^{2+} in ammoniacal media; B-ditto as in A but with gelatin added.

2. E - t Curves Obtained by Means of A Heyrovsky Oscillographic Polarograph.

Heyrovsky studied the reversibility and irreversibility of electrode reactions by means of voltage-time curves [11, 23, 25, 34, 37, 38]. If a reaction is rapid enough and is reversible as in the reduction of cadmium, lead, and thallium ions in 1 N KCl or in HNO_3, then the cathode and anode steps are found to occur at the same potential; as a result a symmetrical curve of the type shown in Fig. 26 A is obtained. The dotted line represents the E - t curve obtained before addition of the depolarizer. The width of the step is a function of depolarizer concentration. When the reaction is irreversible an unsymmetrical E - t curve is obtained in which the step occurs at a more positive potential on the anode branch of the curve than on the cathode branch. The reduction of Zn^{2+} on a dropping mercury cathode in KCl, NH_4OH, or KOH (Fig. 26 B) is an example of an irreversible electrode reaction.

TABLE 6

Reversible Reactions

Element	Supporting electrolyte	Electrode reaction
Cu^{2+}	1 N NH_4OH + 1 N NH_4Cl	$Cu^{2+} + e \rightleftharpoons Cu^{+}$
Cu^{+}	1 N NH_4OH + 1 N NH_4Cl, 1 N KCl	$Cu^{+} + e \rightleftharpoons Cu$
Sb^{3+}	1.0 N HCl	$Sb^{3+} + 3e \rightleftharpoons Sb$
Bi^{3+}	1.0 N HCl	$Bi^{3+} + 3e \rightleftharpoons Bi$
Sn^{2+}	2 N $HClO_4$ + 0.5 N HCl	$Sn^{2+} + 2e \rightleftharpoons Sn$
Pb^{2+}	1.0 N KCl; 1.0 N NaOH; 1 N KCN	$Pb^{2+} + 2e \rightleftharpoons Pb$
U^{6+}	1 N KCl	$U^{6+} + e \rightleftharpoons U^{5+}$
Tl^{+}	1 N KCl; 1 N HCl; 1 N NaOH	$Tl^{+} + e \rightleftharpoons Tl$
In^{3+}	0.1 N KCl; 1 N KCl	$In^{3+} + 3e \rightleftharpoons In$
Cd^{2+}	1 N KCl; 1 N HCl; 0.1 N KCl; 0.1 N HCl	$Cd^{2+} + 2e \rightleftharpoons Cd$
Cr^{3+}	0.1 N KCl	$Cr^{3+} + e \rightleftharpoons Cr^{2+}$
Fe^{3+}	0.1 N KCl	$Fe^{3+} + e \rightleftharpoons Fe^{2+}$
Ni^{2+}	1 N KCN	$Ni^{2+} + 2e \rightleftharpoons Ni$
Co^{2+}	1 N KCN	$Co^{2+} + 2e \rightleftharpoons Co$
Mn^{2+}	0.5 — 1 N KCN	$Mn^{2+} + e \rightleftharpoons Mn^{+}$
Na^{2+}	0.1 N $N(CH_3)_4Cl$ or 0.1 N $N(CH_3)_4OH$	$Na^{+} + e \rightleftharpoons Na$
K^{+}	0.1 N $N(CH_3)_4Cl$ or 0.1 N $N(CH_3)_4OH$	$K^{+} + e \rightleftharpoons K$

TABLE 7

Irreversible Reactions

Element	Supporting electrolyte	Electrode reaction	Difference in value between $E_{1/2}$ on cathode and anode brancnes of curve	Slow electrode process
Cu^{2+}	0.1 N Na_2SO_4; 0.1 N KNO_3	$Cu^{2+} + 2e = Cu$	Observed	-
Bi^{3+}	0.3 M tartrate or citrate pH 4.5	$Bi^{3+} + 3e = Bi$	Observed	-
In^{3+}	0.1 N $HClO_4$	$In^{3+} + 3e = In$	Observed	-
Cd^{2+}	1 N KCN	$Cd^{2+} + 2e = Cd$	-	+
Sn^{2+}	1 N H_2SO_4	$Sn^{2+} + 2e = Sn$	-	+
Co^{2+}	1 N KCN	$Co^{2+} + 2e = Co$	-	+
Co^{2+}	0.1 N KCl	$Co^{2+} + 2e = Co$	-	anode
Zn^{2+}	1 N NH_4OH + 1 N NH_4Cl	$Zn^{2+} + 2e = Zn$	Observed	-
Ni^{2+}	0.1 N KCN	$Ni^{2+} + 2e = Ni$	-	+
Ni^{2+}	$(CH_3)_4NBr, CN^-, Cl^-$	$Ni^{2+} + 2e = Ni$	-	anode
Mn^{2+}	1 N KCl; 1 M NH_4OH+1 M NH_4Cl	$Mn^{2+} + 2e = Mn$	Observed	anode
Fe^{2+}	0.1 N KCl	$Fe^{2+} + 2e = Fe$	Observed	anode
Cr^{2+}	0.1 N KCl	$Cr^{2+} + 2e = Cr$	Observed	-
Al^{3+}	0.1 N LiCl	$Al^{3+} + 3e = Al$	-	anode
In^{3+}	0.1 N HCl	$In^{3+} + 3e = In$	-	cathode
Eu^{3+}	no supporting electrolyte	$Eu^{3+} + e = Eu^{2+}$	-	+
Ti^{4+}	0.1 N HCl	$Ti^{4+} + e = Ti^{3+}$	-	+
IO^{3-}	0.1 N KOH 0.1 N H_2SO_4	$IO^{3-} + 6e = I^-$	-	+
CH_3NO_2	acetate buffer	$-NO_2 + 4e = =-NHOH$	-	no anode wave
$C_6H_5NO_2$	acetate buffer	$-NO_2 + 4e = =-NHOH$	-	no anode wave

By means of E – t curves Heyrovsky studied reduction mechanisms for thallium, lead, cadmium, tin, bismuth, antimony, indium, chromium, manganese, iron, cobalt, nickel, and copper on a dropping mercury cathode. The reversibility of the reactions of many organic materials was also studied. E.g., Heyrovksy showed that maleic acid is reduced irreversibly on the dropping mercury cathode. Heyrovsky also used a streaming mercury electrode [25], for studying reversibility and irreversibility of electrode processes.

Using the results of a study of the reversibility and irreversibility of certain electrode processes we have listed in Table 6 those reactions which were found to be reversible by an oscillographic method. Table 7 contains a list of those reactions which were found to be irreversible according to the oscillographic method. The speed with which the reaction proceeds on the surface of the mercury electrode is of essential importance in the case of irreversible electrode reactions. A decision as to whether or not a reaction is slow or fast can be made from a comparison of the rates of the two reactions. When the reaction velocity of the same electrically

Fig.26 Voltage - time (E - t) curves.
A - for a reversible reaction;
B - for an irreversible reaction

reduced material in different supporting electrolytes varies, e.g. the rate at which nickel is reduced in a solution of KCN is greater than the rate at which it is reduced in KCl, then the first reaction can be regarded as fast and the second, slow.

When the reaction velocity of the two different electrically reduced materials in the same supporting electrolyte differ considerably from each other, e.g. cadmium in KCl is reduced considerably more rapidly than cobalt in KCl, then the cadmium reaction can be regarded as fast and the cobalt reaction as slow.

Table 7 includes two additional columns; one of them contains information as to whether or not there is a difference in the potentials on the cathode and anode branches of the curve; and in the other information as to which reaction is the slower. If both reactions are slow (anode and cathode) then a plus sign is given in this column. If one is slower than the other, then information is given as to which reaction is the slower.

SUMMARY

1. Original designs of oscillographic polarographs by means of which various oscillographic curves can be obtained are discussed: I - E, E - t, dE/dt - t.

2. The respective equations of Randles and Seveik for the maximum current are considered. It has been shown that the experimental results do not agree with the values of the maximum current calculated by means of Randles' and Seveik's equations, respectively, when using saw-tooth voltage conditions. Seveik's equation can be corrected when operating under impluse conditions.

3. A new equation is suggested for the maximum current; this equation only holds for saw-tooth voltage operating conditions.

4. It has been shown that it is possible to establish the qualitative composition of a solution and to carry out quantitative determinations of inorganic and organic compounds by means of oscillographic polarography.

5. It has been shown that it is better to study the reversibility and irreversibility of electrode reactions by means of oscillographic polarography rather than by ordinary polarography.

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A FLAME PHOTOELECTRIC METHOD FOR THE DETERMINATION OF CALCIUM IN SOLUTION

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The acetylene-air flame excites radiation from only a limited number of elements. The spectrum consists of a few lines, the wave-lengths of which differ considerably from each other. This fact permits a comparatively easy separation of the characteristic radiation of some elements by means of light filters. The intensity of the radiation isolated can be measured photoelectrically and is a function of the concentration of the element fed into the flame. The fact that the burning conditions of the flame are steady, and the steady rate at which test material can be fed into the flame as a solution, permit one to carry out analysis by means of the absolute intensity of the radiation.

The author has previously described [1], a quantitative method for the determination of sodium and potassium in soils in which light filters are used as follows. Using an atomizer and a burner (Fig. 1) the test solution is fed into the flame. The radiation of sodium 5890/95 A and potassium 7665/99 A are isolated with filters with maximum transmission at the wave length of the radiation being measured.

The isolated sodium radiation falls on a selenium photo-element while that of the potassium falls on a sulfide-silver element. The photo-current is measured with a mirror galvanometer with a sensitivity of $10^{-8} - 10^{-10}$ A. The concentration of test element can be measured from 1 mg/liter or $1 \cdot 10^{-4}$% upwards of test solution by means of calibration curves.

It has been shown that the presence of aluminum, iron, and magnesium in the test solution in amounts of 0.1% have practically no effect on sodium and potassium determinations. Neither does potassium interfere with sodium determinations and vice-versa. The presence of calcium in solution however does lead to high results for sodium and to a lesser extent for potassium. This interference on the part of calcium has been noted by a few authors [2, 3, 4, 5], who recommend removal of calcium from solution or application of suitable corrections.

The high values obtained for sodium and potassium are the result of the rather wide and intense bands of calcium with maxima at 5500 A and 6150 A, and insufficiently complete separation by the light filters. The filter not only transmits the radiation of the test elements but also that of the bands and background of calcium so that the photo-current measured is a sum of various photo-currents.

This fact necessitates taking this additional photo-current of calcium into account, and compensating for it as follows.

A filter with maximum transmission at 6200 A is used to isolate the calcium radiation at the bands noted above. The isolated radiation is directed on to a selenium photo-element which is connected in a direction reversed to that of the

photoelements designed for sodium and potassium determinations (Fig. 2). It is thus possible to compensate the photocurrent caused by calcium when the filters used for sodium and potassium determinations are not sufficiently monochromatic, by opposing to this current another one from an isolated calcium band. In practice this is achieved as follows.

A solution of calcium free from sodium and potassium is fed into a flame. By adjusting a diaphragm on the compensator filter a galvanometer reading is obtained at which there is no change whether calcium is fed into the flame or not. This position is the "null" point; it is not changed during an analysis. The calcium content should be roughly the same as in the test solution.

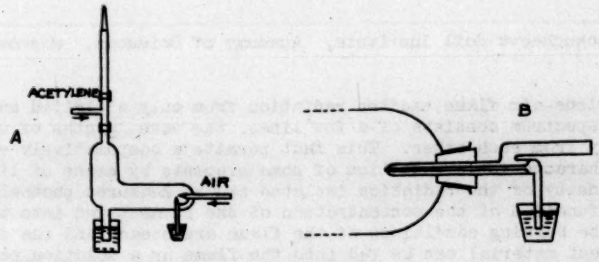

Fig. 1 A) Atomizer and burner; B) part of the atomizer with an injector of another type.

The Ca-filter is not completely monochromatic either, and does transmit Na and K radiations to some extent. By compensating through using the diaphragm it is possible to get conditions under which practically no Na and K radiation is transmitted. This is also true of the Na-filter and the K-filter when it is necessary to compensate for Na and K during Ca determinations.

Tests showed that the calibration curves for sodium and potassium constructed by means of the pure solutions or with solution containing calcium (500 mg/liter) coincide entirely, starting from concentrations of 1 mg/liter of the test element. The accuracy of sodium and potassium determinations in the concentration range 1–100 mg/liter is ca. $\pm$ 5%.

The general appearance of the set-up is shown in Fig. 3.

It is natural that the question of determining calcium on the same set-up arises. Calcium gives a very strong line at 4227 A in the flame, and two bands with maxima in the regions 5500 and 6150 A. The absence of suitable photoelements means that the fundamental line cannot be used, while a comparison of the bands showed that by using the latter band a considerably higher sensitivity can be achieved.

In order to isolate the red calcium band a light filter with maximum transmission at 6200 A was used; the isolated radiation was directed on to a selenium photoelement. The photo-current was measured using a mirror galvanometer with a sensitivity of $10^{-9} - 10^{-10}$ A.

Accurate quantitative determinations of solutions containing 5 mg/liter were shown to be possible. The calibration curve is a straight line up to concentrations of calcium of 4000 mg/liter. Further study showed that quantitative determination of calcium in solution is accompanied by difficulties which are closely related to the intensity of the calcium radiation when other cations and

anions are present in solution. These difficulties are either usually not met with at all or present little trouble in determinations of sodium and potassium.

In our tests we found that calibration curves made with the help of pure solutions of $CaCl_2$ and $CaSO_4$ at concentrations from 5 - 400 mg/liter coindide with each other, but the radiation from calcium as $CaHPO_4$ is considerably less over the same concentration range.

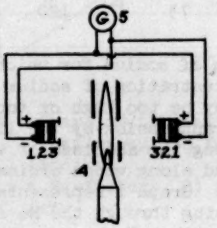

Fig. 2. Method of connecting up: 1) photo-elements; 2) light filters; 3) additional diaphragms; 4) cylindrical diaphragms; 5) galvanometer.

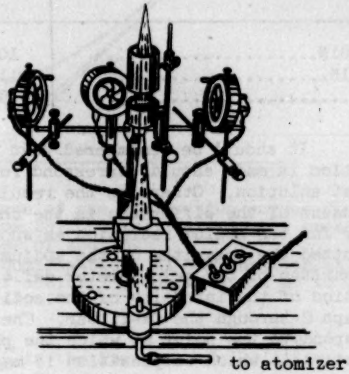

Fig. 3. General appearance of the set-up.

The relation between the radiation from calcium and the character and concentration of the acid in which the calcium salt is dissolved is of great practical interest, therefore. We took 100 mg/liter of calcium as $CaCl_2$, which was then dissolved in four acids of various concentrations. Their calcium contents were determined by means of calibration curves drawn up with the aid of aqueous solutions of $CaCl_2$. The results obtained are given in Table 1.

From these results it is evident that on increasing the concentration of H_2SO_4 and HNO_3 the radiation intensity of the calcium decreases, while in the case of acetic acid it increases; in the case of hydrochloric acid behavior is haphazard[1]). In soil analysis determinations in hydrochloric acid solutions are of practical importance. It should be pointed out that if the hydrochloric acid concentration does not exceed 1%, the analysis can be carried out using aqeous standards and vice-versa. In general the nature of the acid used and its concentration should be taken into account when carrying out an analysis.

Further tests showed that high results are obtained for calcium when sodium is present in solution. In order to avoid this, the compensation method developed above for sodium is used.[2])

1) Solutions were prepared and analyzed several times.
2) According to the location of the maximum transmission of the Ca-filter and the width of the transmission band it may be also necessary to compensate for potassium.

TABLE 1

Relation between Intensity of the Calcium Radiation and the Nature and Character of the Acid Used.

Acid Concentration	Acid			
	HCl	H_2SO_4	HNO_3	CH_3COOH
0.01N.....	104	78	87	96
0.1N.....	110	67	80	100
1N.....	93	58	73	120

It should be remembered that the concentration of sodium for which compensation is made should correspond roughly to the concentration of sodium in the test solution. Otherwise the results for calcium may be too high or too low because of the difference in the character of the transmission by the light filter for the sodium rediation as shown in Fig. 4, along the abscissa of which is plotted the logarithm of the sodium concentration, and along whose ordinate the logarithm of the galvanometer deflection is plotted. Graph 1 represents the relation of the intensity of the sodium radiation passing through the Na-filter, and Graph 2 through the Ca-filter. The point of intersection of the two curves corresponds to the point at which the photo-currents are equal and the sodium concentration at which compensation is made. It follows from this that if the sodium concentration in the test solution is lower than the concentration at which compensation is made, then the reqults for calcium will be low and vice-versa.

In practice, up to a limit of 100 mg/liter of sodium, it is possible to compensate for the effect of sodium at one sodium concentration, e. g. 500 mg/liter; the overwhelming majority of soil analyses lie within these limits, except total calcium analysis after fusion and analysis of some other specific materials. It is not essential to know the exact amount of sodium in solution; it can be determined approximately on the same apparatus.

Fig. 5 illustrates calibration curves for calcium in the presence of 10 mg/liter of sodium and for various compensation concentrations of sodium.

Table 2 contains results of the analysis of aqueous solutions of $CaCl_2$ in the presence of 10 g/liter of sodium as NaCl and Na_2SO_4. The concentration of sodium is similar to that in the solutions obtained after fusion of the soil with soda. Aqueous solutions of $CaCl_2$ were used as standards.

The results are of two fold interest:

1) The difference between the concentrations of calcium obtained with and without compensation is almost constant. In the presence of Na_2SO_4 this difference on an average amounts to 26 mg, while in the presence of NaCl it is 30 mg. The high values obtained when no compensation is made is caused by the presence in solution of sodium which gives a considerable background in the flame, and inefficient separation on the part of the Ca-filter (it is possible that the sodium salts are contaminated with calcium salts). Compensation for all concentrations of calcium is effected by subtracting equal amounts from the fictitious concentration obtained as the result of the presence of sodium ions in solution.

2) On increasing the calcium concentration there is observed a decrease in the values actually found for it and this decrease increases with relatively increasing concentration. This decrease is clearly defined in the presence of Na_2SO_4 and is also noticeable in the presence of NaCl. This phenomenon apparently depends on the nature of the anion linked with the sodium. Some results which

illustrate this point are given.

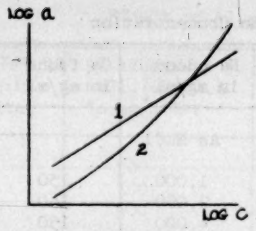

Fig. 4. Shape of the calibration curves for sodium;
1) for a Na-filter; 2) for a Ca-filter.

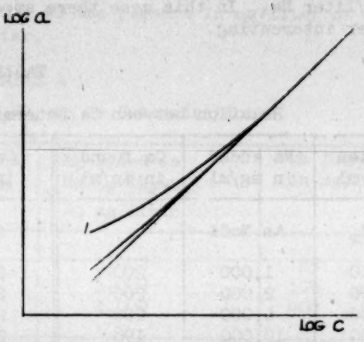

Fig. 5. Shape of the calibration curves for calcium (from 25-1000 mg/liter) in the presence of 10 g/liter of sodium.
1) Without compensation; 2) compensation at 4 g/liter of sodium; 3) compensation at 10 g/liter of sodium.

TABLE 2

Analysis of Aqueous Solutions of $CaCl_2$ in the Presence of 10g/liter of Na as NaCl and Na_2SO_4

Ca taken in the form of $CaCl_2$	Ca found in mg			
	In the presence of Na_2SO_4		In the presence of NaCl	
	with compensation	without compensation	with compensation	without compensation
Ca 5 mg/liter + Na 10000mg/l	5.2	32.0	5.5	36.5
10 " + Na 10000 "	10.5	37.0	11.0	42.0
20 " + Na 10000 "	21.0	47.0	21.5	52
40 " + Na 10000 "	40.0	65.0	42.0	72
100 " + Na 10000 "	85.0	112.0	100.0	130
200 " + Na 10000 "	150.0	175.0	198.0	230
400 " + Na 10000 "	260.0	285.0	385.0	415

The results in Table 3 illustrate the relationship between calcium determined both as $CaCl_2$ and $CaSO_4$, and the sodium concentration; sodium is present as NaCl and Na_2SO_4.

These results show that in mixtures of $CaCl_2$ + NaCl the concentrations of calcium found agree with the original concentrations. The tendency observed earlier toward a decrease in the concentration actually found for calcium on increasing its concentration in the solution of the test mixture must not be forgotten.

In mixtures of $CaSO_4$ + NaCl, $CaCl_2$ + Na_2SO_4 and $CaSO_4$ + Na_2SO_4 there is a sharp decrease in the concentration found as compared with the initial concentration. What apparently gives rise to this decrease in the concentration determined for calcium is the presence of the SO_4^{2-} ions in the salt solution. The

maximum decrease in concentration found for calcium occurs in the presence of 2 – 4 g/liter Na. In this case there appears to be a point of inflexion which is rather interesting.

TABLE 3

Relation between Ca Determined and Na Concentration

Ca taken in mg/ml	Na added in mg/ml	Ca found in mg/ml	Ca taken in mg/ml	Na added in mg/ml	Ca found in mg/ml
As $CaCl_2$	As NaCl		As $CaSO_4$	As NaCl	
200	1,000	200	200	1,000	150
200	2,000	200	200	2,000	140
200	4,000	200	200	4,000	150
200	10,000	198	200	10,000	184
	As Na_2SO_4			As Na_2SO_4	
200	1,000	140	200	1,000	126
200	2,000	117	200	2,000	120
200	4,000	118	200	4,000	125
200	10,000	150	200	10,000	155

Results on the effects of aluminum, magnesium, and sulfuric acid [1] in solution on calcium determinations are of considerable interest. These results are given in Table 4.

The results given in Table 4 show that the intensity of the calcium radiation falls sharply in the presence of aluminum. This decrease in intensity is greater the lower the calcium concentration and the greater the aluminum concentration. There is a particularly large decrease in intensity when calcium, aluminum, and sulfuric acid or, more accurately, SO_4^{2-} ions are all present simultaneously in solution. When hydrochloric and nitric acids are added to the solution instead of H_2SO_4 the decrease is not observed.

When $CaCl_2$ and $MgCl_2$ are present at the same time the results found for calcium are somewhat high; this may be the result of the superposition of the magnesium band, or even more probably the result of contamination of the magnesium salts with calcium salts. In soil analysis any effect shown by magnesium will be absent in the overwhelming majority of analyses because of its low concentration. When materials having a high concentration of magnesium are analyzed possible interference on the part of magnesium must be borne in mind and corrected for in accordance with the actual conditions of analysis.

Further, the results in Table 4 show that the intensity of the calcium radiation when both magnesium and sulfuric acid are present in solution is strongly depressed, but to a smaller extent than when aluminum is present; the effect becomes more marked with increasing calcium concentration. We established that $MgSO_4$ in solution leads to a considerable lowering of the results for calcium determinations (these results are not given in this article).

The results given in Table 5 clearly demonstrate the special role played by Al^{3+} and SO_4^{2-} when both are present together. All the solutions are hydrochlo-

1) The concentration of sulfuric acid is 5 ml/liter of solution.

ric solutions (HCl 8%), all the salts are hydrochlorides, the number after the symbol for the element denotes the amount of the element in mg/liter of solution. 0.2 ml of H_2SO_4 is added per liter.

TABLE 4

Effect of Al, Mg, and H_2SO_4 on Ca Determinations

Ca taken as $CaCl_2$, in mg/liter	Al added as $AlCl_3$ ($+H_2SO_4$), in mg/liter	Ca found, in mg/l	Mg added as $MgCl_2$ ($+H_2SO_4$) in mg/liter	Ca found in mg/liter
20	500	11	1,000	23
100	500	75	1,000	104
400	500	340	1,000	400
20	500 + H_2SO_4	0	1,000 + H_2SO_4	21.5
100	500 + H_2SO_4	4.4	1,000 + H_2SO_4	95
400	500 + H_2SO_4	52	1,000 + H_2SO_4	250
200	200	165	200	200
200	500	155	400	200
200	1,000	145	1,000	205
200	200 + H_2SO_4	46	200 + H_2SO_4	115
200	500 + H_2SO_4	14	500 + H_2SO_4	130
200	1,000 + H_2SO_4	5	1,000 + H_2SO_4	165

The information given above shows that both cations and anions present in solution can affect calcium determinations. High results for calcium in the presence of sodium is a consequence of a simple superposition of the wide and intense background of sodium, the possible appearance of sodium radiation at 6154/61 A, and inefficient light filters. This may be overcome by compensation. It will be of less importance also when better light filters are used.

Low results for calcium or what boils down to the same thing, a decrease in intensity of its radiation when Al^{3+} and SO_4^{2-} ions are present, particularly when present together, owe their origin to something entirely different; the low results are related to complex physico-chemical processes occurring in the flame, and probably with the formation of new, stable molecular compounds, which depress the number of free atoms in the flame zone.

A decrease in intensity is observed not only for the calcium band at 5,500 and 6,200 A (this can be observed visually) but even for the fundamental line 4,227 A, as we established by separating this line with a monochromator and measuring its intensity with a photoelectric multiplier.

Possibly Ca^{2+} and Al^{3+} ions are oxidized in the flame to give CaO and Al_2O_3, which then react at the high temperature of the flame to give stable compounds-calcium aluminates of the type $CaAl_2O$ and $Ca_3Al_2O_4$. It is possible that SO_4^{2-} favors oxidation of the cations and formation of aluminates or other more complex and stable compounds.

That calcium and aluminum do react can be confirmed by calcining them. In the presence of sulfuric acid the reaction is considerably more rapid though the reaction product outwardly differs somewhat from that obtained in the absence of sulfuric acid.

Let us consider the analytical results for calcium in various materials. Table 6 contains results on the analysis of aqueous extracts of soils. Analysis was carried out on the basis of aqueous standard solutions of $CaCl_2$ and using the band at 6200 A. The samples contained up to 300 mg of sodium /liter. Results for calcium are practically the same with and without compensation for 100, 200, and 300 mg of sodium /liter.

TABLE 5

Effect of Cations and Anions in Solution on Ca Determinations

Ca taken, in mg/l	Element added and its amount, in mg/l	Ca found, in mg/l	Relative error, in %
100	Mg 25, Fe 50, K 40, Na 100, HCl, H_2SO_4	62	−38
200		110	−45
400		175	−56
100	Ditto + Al 150	9	−91
200		31	−84
400		140	−66

TABLE 6

Results of the Analysis of Aqueous Soil Extracts

Sample No.	Method		Deviation, in %
	Photometric.	Chemical.	
1	10.6	10.0	+ 6.0
2	24.7	26.0	− 5.0
3	26.0	27.9	− 6.8
4	29.0	32.0	− 9.4
5	30.6	32.0	− 4.4
6	70.0	66.8	+ 4.8
7	187.0	230.0	−19.0
8	191.0	248.0	− 23.0
9	276.0	269.0	+ 2.6
10	440.0	447.0	− 1.5
11	468.0	480.0	− 2.5

The mean arithmetic deviations of the results adduced is ± 8%. There is an obvious tendency toward low results for calcium. Samples 7 and 8 are extracts from salt soils containing considerable amounts of SO_4^{2-} ions. After a five-fold dilution the final results obtained were 225 and 242 mg/liter, respectively, which were in godd agreement with chemical analysis. The mean deviation is lowered to ± 4.3%.

Results which are low by as much as 25% of the calcium present were obtained during the analysis of strongly mineralized soil waters; better results were obtained when they were diluted.

Thus analysis of aqueous (and other) extracts for calcium on the basis of pure aqueous standard solutions of calcium can lead to systematically low results for calcium. The composition of the standard calcium solutions should reflect that of the test samples.

Table 7 contains results on the determination of calcium in soils fused with soda and subsequently dissolved in water. A characteristic of these solutions is the presence of large amounts of sodium (up to 10g/liter) and the acid character of the solutions (ca. 4% HCl); two types of standards were used: 1) 10g/liter of sodium (as NaCl) was added to acid solutions of $CaCl_2$ and 2) the same solutions containing Al 300, Mg 50, Fe 100, K 80 mg/liter (all chlorides). The first four samples were analyzed by means of both standards.

The results given in Table 7 show that soils cannot be analyzed for total calcium using standards of the first type (they do not correspond in composition to that of the test samples) and that accurate results can be obtained when standards with compositions approximate to that of test samples are used. Of interest is the determination of total calcium in soil after decomposition with HF (large amounts of sodium are absent). Decomposition is usually carried out in the presence of H_2SO_4. Analysis of the solution obtained gave considerably lower

results than those obtained for soils which were fused.

TABLE 7

Determination of Total Calcium in Soils After Soda Fusion

Sample No.	Method		Deviation, in %	Notes
	Photometric	Chemical		
1	5.1	8.1	-37.2	First type of standard
2	5.4	8.6	-37.0	
3	5.5	9.1	-39.3	
4	6.0	10.0	-40.0	
1	8.5	8.1	+ 4.9	Second type of standard
2	8.5	8.6	- 1.2	
3	9.2	8.1	+ 1.1	
4	10.0	10.0	0	
5	8.0	8.0	0	
6	8.4	8.3	+ 1.3	
7	8.7	8.1	+ 7.8	
8	8.9	8.9	0	
9	7.8	7.5	+ 4	

TABLE 8

Results of Calcium Analyses of Plant Ash

Sample No.	Method		Deviation, %
	Photometric	Chemical	
1	5.7	5.1	+11.8
2	8.2	8.5	- 3.4
3	9.2	9.5	- 3.2
4	16.5	15.5	+ 6.5
5	21.7	21.1	+ 2.9
6	18.6	19.2	- 3.1
7	22.5	21.1	+ 3.6
8	7.4	7.7	- 3.9
9	9.1	9.6	- 5.2

Decomposition in the presence of HCl takes very long and is difficult. Here it is also possible to get incomplete decomposition and the formation of very stable compounds of CaF_2. Results of chemical analysis of solutions obtained by this method were so conflicting that they could not be compared with results obtained photometrically.

Table 8 contains results on the calcium content of plant ash. The plants were ashed and the ash washed with dilute HCl; after dilution a weak acid solution was obtained. Analysis was carried out using aqueous solutions of $CaCl_2$ as standards.

These results show that plant ash can be analyzed for calcium using aqueous $CaCl_2$ standards. For this type of analysis the sodium content was so low that there was no need for compensation. One must however bear in mind the possibility of a large increase in the amount of some elements in plant ash because of the plants' selective action and the large amounts of certain elements in soils and fertilizers. In such cases the standard solution must have a composition similar to that of the test solutions and compensation may be essential.

SUMMARY

1. By means of a flame-photometric method calcium can be determined in solution by means of its characteristic radiation at 6200 and 5500 A, the radiation being isolated by interference light filters. When a selenium photoelement is used the sensitivity of the method is considerably greater for the first band than for the second.

2. Pure $CaCl_2$ and $CaSO_4$ solutions of equal concentration give equally intense radiation. The radiation from calcium as $CaHPO_4$ in solutions of the same calcium concentration is considerably smaller.

3. The accuracy of calcium determinations depends on the other cations and anions present in solution. There is a considerable decrease in radiation intensity for calcium when both Al^{3+} and SO_4^{2-} are present in solution. Interference from sodium can be compensated for.

4. The concentration of sodium at which compensation is carried out should approximate to the concentration of sodium in the test solution.

5. The composition of synthetic standards must approximate as closely as possible to the composition of the test solution.

Solution with various calcium concentrations established by chemical methods should be used as standards.

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QUANTITATIVE COLORIMETRIC DETERMINATION OF ALIPHATIC ALCOHOLS IN THE ULTRA VIOLET

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The problem of determining aliphatic alcohols quantitatively at low concentrations has not yet been satisfactorily solved. Most of the methods published for the quantitative determination of alcohols are only applicable at conentrations of 10^{-3} - 10^{-2}% and higher.

Thus quantitative determination of alcohols by oxidation with potassium bichromate or permanganate [1-4], is only possible at alcohol concentrations greater than 10^{-2}% and the accuracy is not very good at that, since calculation of alcohol content is based on the equation:

$$3R{\cdot}CH_2OH + 8H_2SO + 2K_2Cr_2O_7 = 3R{\cdot}COOH + 2Cr_2(SO_4)_3 + 2K_2SO_4 + 11H_2O.$$

Further oxidation of the acids obtained is ignored [5]. Moreover the analysis is complicated by the presence of other materials of a reducing nature [2].

The sensitivity of Fischer's [6], and Pondorf's [7], methods respectively do not exceed 10^{-2}%. Ketslakh and Pigulevsky [8], noted when using their methods considerable deviations in reaction velocities for the formation of alkylnitrites of various aliphatic alcohols, which hinder the application of the methods for analysis of mixtures containing a mixture of several alcohols.

Zerevitinov's method [9], is applicable for alcohol concentrations of 10^{-3}% and higher; it can, however, only be used for the analysis of absolutely dry materials.

Verley's method [10], which is based on acetylation of the alcohols is only applicable for concentrations of alcohol from 10^{-2}% upwards.

The most sensitive methods for the quantitative determination of alcohols are Vorokhobin's method [11], according to which the alcohol is oxidized with potassium bichromate and the test solution colorimetrically measured by means of the green color of trivalent chromium, and Nizovkin's colorimetric method [12].

Vorokhobin's method according to the author himself permits quantitative determination of ethyl alcohol at concentrations of $5{\cdot}10^{-4}$%, upwards and requires careful purification of the test material from all reducing material. Nizovkin's method is applicable to the analysis of test material containing ethyl alcohol in amounts greater than 10^{-4}%; it is however very complicated and considerable losses of alcohol are possible.

In the present investigation we have attempted to use absorption in the ultraviolet by the alkylnitrites formed as the result of the reaction between alcohol and nitrous acid according to the following equation:

$$ROH + HNO_2 = RNO_2 + H_2O.$$

For the quantitative determination of alcohols, Thomson's [13], and Goodeve's [14], results indicated that gaseous aliphatic alkyl nitrites have a clearly defined absorption spectra in the near ultra-violet consisting of narrow bands at 390, 365, 355, 345, 323, 320 mμ. The position of the bands according to Thomson and Goodeve depend to only an insignificant extent on the chemical nature of the radical R.

Measurements which we made on the absorption spectra of ethyl nitrite, propyl nitrite, and octyl nitrite dissolved in gasoline on the SF-11 spectrophotometer showed that the forms of their spectra is independent of the nature of the radical. All the alkyl nitrites mentioned have a wide absorption band at 400-320 mμ, with maxima at 380, 355, and 345 mμ.

The shape of the absorption curves obtained for the alkyl nitrites shown in Fig.1 and the appreciable value of the absorption coefficient which is $10^2 cm^2/mol$ at 355 mμ indicate that the use of absorption spectra of the alkyl nitrites for colorimetric determination of alcohols is sound. Experiments were accordingly carried out on the colorimetric determination of aqueous solutions of the following alcohols: methyl-, ethyl-, n-propyl-, isopropyl-, n-butyl-, isobutyl-, n-octyl- alcohols, and methylhexylcarbinol, using the following technique; test material containing the alcohol is treated with nitrous acid and the alkyl nitrite formed extracted with gasoline; the extract is placed in a cuvette with quartz windows and then colorimetric determinations carried out with a differential adsorptiometer designed for working in the ultra-violet [15].

Standards were prepared by dissolving aliquots of the alcohols in water using ampoules weighed to an accuracy of 0.02 mg. The alcohols were distilled beforehand and dehydrated, either over freshly calcined copper sulfate or over potash and then distilled over metallic calcium.

Tests were prepared for colorimetric determination as follows: 20 ml of aviation gasoline (washed several times with sulfuric acid d = 1.84 and distilling in the range 35-100°) was introduced into a 50-60 ml separating funnel; this was followed by 20 ml of test solution and 1 ml of 5 N HCl.

2 ml of 25% aqueous sodium nitrite was then added rapidly to the contents of the funnel by means of a pipet with a wide tip, the funnel was then stoppered and shaken thoroughly for 5 minutes.

When the two layers had separated the water was run off while the upper gasoline layer containing the alkyl nitrite was run into a second separating funnel containing 20 ml of aqueous 10% sodium bicarbonate (or 0.1 N NaOH). After a 5 minute period of shaking to free the gasoline layer of alkyl nitrite from nitrogen oxides, the gasoline was rapidly transferred to a cylindrical cuvette with quartz windows and a colorimetric determination carried out using a cuvette filled with pure gasoline as a standard.

In all our experiments we used water-cooled funnels to cut down as much as possible any loss of volatile alkyl nitrites.

The solutions were colorimetrically determined using light filters operating at 360 mμ [16].

The transmission curve of the light filter used is compared with the absorption curve of the alkyl nitrites on Fig. 1.

Calibration curves for solutions of some of the alcohols we tested are given in Fig. 2. The cuvette length was 2 cm both for drawing calibration curves and for analyzing test samples.

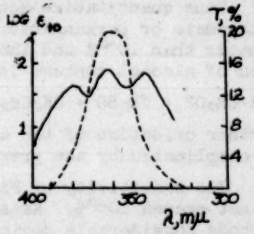

Fig.1. Absorption curve for alkyl nitrites dissolved in gasoline, solid line. Transmission curve for the filter, broken line. T,%-light filter transmission in %. ε_{10}, molar absorption coefficient for the alkyl nitrites.

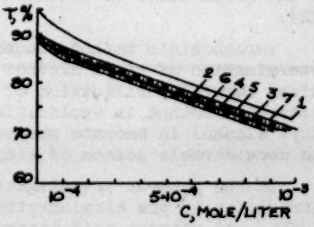

Fig.2. Calibration curves for alcohols:
1- CH_3OH; 2- C_2H_5OH; 3- n-propyl alcohol; 4- isopropyl alcohol; 5- butyl alcohol; 6- isobutyl alcohol; 7- n-octyl alcohol; T%- transmission of solution in % (thickness of layer 2 cm).

As shown in Fig.2 the calibration curves lie close to each other, being arranged on both sides of the curve for n-butyl alcohol. The only anomalous behavior is shown by methyl alcohol; this is probably the result of loss of methyl nitrite on account of its high volatility. Results for the analysis of aqueous solutions of the alcohols listed above are given in Tables 1 and 2.

TABLE 1

Alcohol taken in %	Alcohol found in %	Δc/c in %
Methyl alcohol		
0.0200	0.0202	1
0.0116	0.0110	6
0.0085	0.0086	1.5
0.0058	0.0058	0
0.0030	0.0032	7
0.0022	0.0023	5
0.00085	0.00080	6
Ethyl alcohol		
0.0360	0.0354	2
0.0225	0.0224	0.5
0.00900	0.0096	7
0.00570	0.00530	7
0.00190	0.00175	8
0.00095	0.00085	10.5
0.00080	0.0007	12
n-Propyl alcohol		
0.00605	0.00605	0
0.00403	0.00400	1
0.00200	0.00195	3
0.00150	0.00151	1
0.00130	0.00125	4
0.00110	0.00113	3
0.00060	0.00065	9
0.00050	0.00060	20
Isopropyl alcohol		
0.0375	0.0370	1.5
0.0100	0.0096	4
0.0066	0.0062	7
0.0020	0.0019	5
0.00125	0.00130	4
0.00089	0.00080	11
0.00050	0.00043	14
0.00025	0.00030	20

TABLE 2

Alcohol taken in %	Alcohol found in %	Δc/c in %
n-Butyl alcohol		
0.0300	0.0293	2.5
0.0130	0.0135	4
0.0090	0.0092	2
0.0056	0.0054	4
0.0033	0.0030	10
0.0022	0.0024	9
0.0050	0.0058	16
Isobutyl alcohol		
0.00467	0.00450	3.5
0.00311	0.00300	3
0.00175	0.00170	3
0.00117	0.00105	10
0.00100	0.00089	11
0.00087	0.00080	9
0.00035	0.00029	17
0.00025	0.00027	10
n-octyl alcohol		
0.0317	0.0320	−1
0.0096	0.0090	7
0.0053	0.0048	9
0.0031	0.0032	0
0.0016	0.0015	6
Methylhexylcarbinol		
0.00320	0.00285	11
0.00181	0.00170	6
0.00160	0.00165	3
0.00145	0.00154	6
0.00103	0.00096	7

These results show that when the layer of solution of alkyl nitrite used for colorimetric determination is 2 cm thick, determination can be carried out with a relative error of 1-20%. Quantitative determination can be carried out right down to 10^{-3} - $5 \cdot 10^{-4}$%. A determination takes 20-25 minutes.

Sensitivity can be increased by increasing the thickness of the solution under examination and by cutting down the volume of extractant.

As pointed out above the calibration curves for the various alcohols tested are closely grouped round the curve for n-butyl alcohol. This fact indicates that it may be possible to use the calibration curve for butyl alcohol as a general mean calibration curve for all the alcohols tested; this of course means a

reduction in accuracy, but nevertheless may still be good enough to give an idea of the total content of alcohols in solution.

To check this possibility we carried out analysis of several mixtures of alcohols. Results are given in Table 3.

TABLE 3

Experiment No.	Designation of alcohol	Alcohol taken: Concentration of alcohol in mol/liter	Alcohol found in mol/liter	c/c in %
1	Ethyl	$2.35 \cdot 10^{-4}$	-	-
	Isopropyl	$2.72 \cdot 10^{-4}$	-	-
	Isobutyl	$3.10 \cdot 10^{-4}$	-	-
	Total	$8.17 \cdot 10^{-4}$	$7.23 \cdot 10^{-4}$	11
2	n-Propyl	$1.24 \cdot 10^{-4}$	-	-
	Isobutyl	$0.73 \cdot 10^{-4}$	-	-
	n-Octyl	$2.91 \cdot 10^{-4}$	-	-
	Total	$4.88 \cdot 10^{-4}$	$4.15 \cdot 10^{-4}$	15
3	Ethyl	$2.35 \cdot 10^{-4}$	-	-
	Isopropyl	$1.36 \cdot 10^{-4}$	-	-
	n-Butyl	$0.72 \cdot 10^{-4}$	-	-
	n-Octyl	$1.91 \cdot 10^{-4}$	-	-
	Total	$6.34 \cdot 10^{-4}$	$7.66 \cdot 10^{-4}$	21

SUMMARY

1. The possibility has been demonstrated of carrying out colorimetric determination of aqueous solutions of the following alcohols in the ultra-violet: methyl-, ethyl-, n-propyl-, isopropyl-, n-butyl isobutyl-, n-octyl-alcohols and methylhexylcarbinol. The relative error of determination is 1-20%. The sensitivity of a determination is 10^{-3} - $5 \cdot 10^{-4}$% alcohol in the test material.

2. It has been established that the shape of the calibration curves for the alcohols listed with the exception of methyl alcohol permits quantitative evaluation of the total alcohol content in one solution with a relative error of 11-21%.

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1) See Consultants Bureau Translation, p. 215

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QUANTITATIVE MICRO-DETERMINATION OF CARBON, IN PARTICULAR IN TANTALUM CARBIDE

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A. A Micro-method for Determination of Total Carbon.

Carbon is usually determined quantitatively either gravimetrically, by trapping the gases evolved in absorption flasks filled with askarite and other similar reagents, or gas-volumetrically, using an Orsat type of apparatus. For very accurate gravimetric methods of determining small amounts of carbon, a micro-balance has to be used.

Our aim was to develop a method of determining small amounts of carbon in which an ordinary analytical balance could be used without sacrifice of accuracy, but rather with greater accuracy; this we hoped to achieve by using a method of micro-gravimetric titration worked out by one of us [1].

Acidimetry can be used as a basis for determination of carbon. In our case, however, the problem is complicated by the fact that before titration the CO_2 must be completely removed from the gas mixture after combustion which contains oxygen. We used a standard solution of barium hydroxide to absorb the CO_2; the amount of CO_2 absorbed is determined by back titration of excess barium hydroxide with 0.1 N hydrochloric acid, using phenolphthalein as indicator, the barium carbonate formed being removed beforehand.[1)]

10 mg of carbon is equivalent to 37 mg CO_2; the accuracy possible, therefore, when an ordinary analytical balance is used for gravimetric determination, is ca. 0.5% because of weighing errors. When only 1 mg of carbon is available the accuracy does not exceed 5%.

When a volumetric finish is used 10 mg of carbon is equivalent to 16.6 ml of 0.1 N hydrochloric acid, which can be measured with an accuracy of one drop (0.02 - 0.05 ml), i.e. 0.15 - 0.2%. For smaller amounts of carbon, down to 1 mg C, the same accuracy can be maintained by using weaker standard solutions (0.01 N), or using micro volumetric and particularly ultra-micro gravimetric apparatus.

A combination of these techniques permits determinations of the same order of accuracy with tenths of a milligram of carbon.

This simple method has great possibilities when the carbon content is appreciable, particularly in alloys. A sample of the order of ca. 100 mg can be weighed out accurately enough on a simple analytical balance and its carbon content (ca. 1 mg) can be determined with great accuracy. When such a technique is used it is essential that the gas evolved should be completely absorbed by the standard solution. The use of small porous glass sinters to give a fine stream of bubbles is inadmissible because of the difficulties involved during subsequent titration (and also because of clogging of the pores with barium carbonate); the use of flasks of the Tishchenko and Drexel type does not ensure complete CO_2 absorption when weak solutions are employed.

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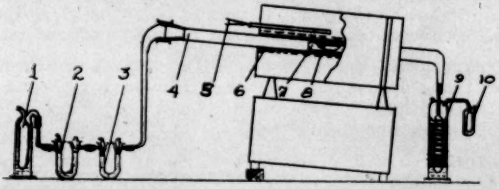
1) Many authors recommend back titration with oxalic rather than hydrochloric acid (in order to avoid partial solution of barium carbonate in cases where there is poor mixing and the local hydrogen ion concentration is sufficient to dissolve the carbonate when hydrochloric acid is used).

We constructed an absorption apparatus (see following article) [2], with a plate type absorption system, each section of which keeps the bubbles in contact with the absorbent solution, and is far more efficient than scrubbers of the Drexel type. The precipitate which forms falls on the plate without blocking the openings. Titration of the solution in this flask presents no difficulty.

The Apparatus Used.

The set-up is schematically shown in the diagramm. Oxygen from a reservoir passes into two flasks connected in series containing sulfuric acid; these are connected to two tubes filled with powdered BaO (KOH, NaOH) and to a tube filled with phosphorus pentoxide. The oxygen next passes into a quartz tube fitted into a combustion oven. Oven and combustion tube are inclined so that the CO_2 flows out into the absorbent side of the apparatus. The quartz tube is connected with the specially constructed scrubber containing absorbent solution for trapping the CO_2 which passes through it with oxygen after combustion. Where necessary the gas can be passed first through an absorbing tower filled with phosphorus pentoxide in order to trap and determine moisture. A standard solution of barium hydroxide (see below) is poured beforehand into the scrubber, which is filled with an inert gas such as argon or oxygen. From this scrubber, the gas proceeds to a control scrubber filled with $Ba(OH)_2$, where the gas is finally tested to see whether or not it is free of CO_2.



1-Scrubber with H_2SO_4; 2- tube with BaO; 3- tube with P_2O_5; 4- quartz tube; 5- platinum-platinum rhodium thermocouple; 6- Mars oven; 7- protective quartz tube; 8- porcelain boat; 9- scrubber with $Ba(OH)_2$; 10- control flask with $Ba(OH)_2$.

Micro Determination of Carbon

The aliquot of carbon-containing material, e.g. graphite, is weighed into a porcelain boat and heated for 19 minutes to the temperature of incipient combustion, in the case of graphite to 600-650°. The amount of oxygen passed through the combustion tube should be approximately four times that of the CO_2 formed. Dilution should not be greater than this during the course of combustion. 20 mg of graphite yields ca. 40 ml of CO_2, so that approximately 160-200 ml of oxygen should be fed into the combustion tube. Oxygen should not be passed into the tube from the reservoir while the temperature is being taken up to 600°, since the amount of it already in the oven should be enough to start off the combustion of graphite (the volume of the tube is 150-200 ml under normal conditions). When the temperature approaches 600°, or even before, the oxygen throughput must be controlled (i.e., the oxygen passing through the scrubbers containing sulfuric acid into the oven) so that it is ca. 3 ml/min. During the subsequent 10 minutes the temperature is raised to 900-950° and is kept at this level during combustion. The oxygen throughput remains unchanged for the first 30-40 minutes and only after the formation and washing of considerable amounts of barium carbonate can the rate be increased to, say, 5 ml/minute. The oven is then switched off and the oxygen passed through at a rate of 20-25 ml/minute for 5-10 minutes to expel

any residual CO_2. The scrubber is disconnected from the combustion tube and a tube for leading in oxygen free from CO_2 connected to its inlet tube. The control flask containing $Ba(OH)_2$ is also disconnected and the outlet tube closed with a glass stopper, etc. The cork of the tube used for leading in the buret tip is then removed and an inert gas passed through; two drops of phenolphthalein are then added and the tip of the buret containing standard HCl introduced. The throughput of the inert gas should be as low as possible; the solution is thereby mixed during titration with HCl in such a way that the solution in the upper part of the titration flask is not colorless, thus indicating that it is not acid and thereby avoiding the danger of $BaCO_3$ dissolving in the HCl and giving erroneous results. If mixing is too rapid as a result of too high a gas throughput there may be mechanical carryover of solution and subsequent errors. The optimum inert gas throughput can be determined in a preliminary experiment. The optimal value can then be easily attained by counting the gas bubbles in the washer, while the color of the indicator in the upper layer serves as a guide[1]. The whole titration usually takes only 15-20 minutes. The acid is added at the rate of 1 ml/minute during the first half of the titration, and more slowly as the end point is reached.

Graphite with a moisture content of 1% was used as test material. The aliquots of carbon used for work with washer No.3 varied from 20-35 mg. The concentration of the barium hydroxide and hydrochloric acid used was 0.2 N. Analytical grade hydrochloric acid was standardized gravimetrically by precipitation of 50 ml of the solution with excess silver nitrate. The accuracy of determination was 0.01%. Barium hydroxide was standardized by titration in an argon atmosphere.

TABLE 1

Determination No.	Weight of carbide	Total carbon found		Ta found from the difference between (2) and (3) calculated as %	Ta_2O_5 found after combustion, in mg	Ta found in the aliquot after calculation from the amount of Ta_2O_5		Mean amount of Ta from (5) and (8), in %	Overall formula
		in mg	in %			in mg	in %		
1	2	3	4	5	6	7	8	9	
1	196.1	10.7	5.45	94.55	227.0	185.9	94.79	94.67	-
2	188.4	9.7	5.20	94.80	218.5	178.9	94.93	94.86	-
3	152.2	7.9	5.19	94.81	174.7	143.0	93.95	94.38	-
		Mean 5.28 ± 0.11				Mean 94.63 ± 0.17			$TaC_{0.84}$

Note. Ta was determined both from the pentoxide formed and from the difference TaC_x (aliquot) − C_{total}.

Experiments showed that the accuracy is limited only by the accuracy with which the graphite is weighed; for graphite weighing 10-30 mg the accuracy lies within the limits of 1% of the weight.

[1] Toward the end of the titration one should cease adding acid from time to time for about half a minute, in order to detach the flask from the buret and, while still passing inert gas through, incline the flask from side to side. When this is done the gas lifts the precipitate off the bottom and stirs up the alkaline layer with the layer on top of it. Slight shaking of the absorption flask will also facilitate this.

For determination of carbon in various compounds and alloys it is expedient to carry out one or two qualitative tests to establish the initial and final combustion temperatures of the materials in oxygen and the optimum rate and amount of oxygen to be passed through the apparatus.

Ca. 200 mg of tantalum carbide was used for determination of total carbon. Combustion and titration were carried out as described above. Results are given in Table 1.

Ultra-Micro Gravimetric Determination of Carbon.

In some instances it is necessary to determine very small amounts of carbon. E.g. the determination of free carbon in tantalum carbide. Having taken a sample of 30-40 mg and separated the combined carbon by a method described below, we filtered off the free carbon, the amount of this came to about 0.2% of the sample, i.e., approximately 100 γ, and in no instance greater than 1 mg. In this case the technique should be modified as follows; the combustion tube used should have a volume of 40-50 cm^3; under no circumstances should rubber connections be used.

Before combustion it is essential to ensure that all carbon dioxide has been desorbed from the tube walls by blowing through oxygen heated to 800° in an oven. This operation decreases titration errors for C (as CO_2) to 40 γ. When the tube has been thus treated the oven is moved on to the boat and combustion carried out as usual. It is essential to carry out blank tests with an empty boat because desorption of CO_2 can be observed here again, although to a smaller extent. In our experiments this amounted to 20γ, so that a constant correction must be applied.

In order to trap CO_2 released by the combustion of 1 mg or less of carbon we made a special washer (see following article) suitable for ultra-micro gravimetric determination. 1-1.5 g of 0.1 R solution of barium hydroxide which was weighed on an analytical balance[1], was introduced into the washer and after CO_2 absorption titrated with a solution of 0.1 R HCl (where 0.1 R is a gravimetrically standardized solution as distinct from 0.1 N) by means of a gravimetric micro-buret described in [1].

B. A Micro Method for the Determination of Free Carbon in Tantalum Carbide.[2]

A mixture of hydrogen fluoride and nitric acid was used to dissolve the tantalum carbide. Normally a solution containing a high percentage of hydrogen fluoride is used, but this may give rise to some difficulties when carrying out the analysis.

We tried to find the minimum concentration of HF and the minimum ratio of $HF:HNO_3$ which would ensure that solution of the carbide would be rapid and complete.

As a result of our investigations we developed the following micro method. 30-50 mg of tantalum carbides [3], from $TaC_{0.38}$ to $TaC_{0.92}$ containing 2-6 weight % (i.e. 1-2 mg) of total carbon and approximately 0.2 to 0.8% (i.e. 0.1 - 0.4 mg) free carbon is weighed out into an 8 ml platinum crucible and wetted with 0.5 ml of water; 1 ml of a mixture of chemically pure undiluted hydrogen fluoride and nitric acid (in a ratio of 1:5) is then added. The crucible is heated on a water bath for 15 minutes, whereupon the combined carbon (carbide) dissolves completely. The crucible is then almost

1) The theoretical basis and the technique of gravimetric titration have been developed in Ormont's article [1].

2) Yu. K. Egorova participated in this work

filled with distilled water, a quartz filter stick is placed in the liquid surface, and the liquid sucked up by means of a water pump.

The concentration of hydrogen fluoride is too low to attack the quartz filter seriously, and such a filter does away with the use of asbestos filters which can be a source of large errors. The crucible is filled up again with hot distilled water and the liquid filtered off. Washing is continued to neutral reaction, after which the crucible together with precipitate and filter in which some of the carbon is stuck are dried in an oven; all the latter are then heated in a tubular combustion oven and the CO_2 evolved absorbed in 0.2 N barium hydroxide as described above.

It is best to determine carbon in such small amounts by the method of gravimetric ultra-micro titration [1].

It was established that free graphite is practically insoluble in the $HF + HNO_3$ mixture, and that in any case the decrease in free carbon content as a result of interaction with reagent does not exceed 1% of the absolute amount; the latter amounts to 10% of the total carbon. For an average total carbon content of ca. 5% in a sample, the amount of free carbon present does not exceed ca. 0.5%.

This method is accordingly capable of giving a high overall accuracy, of the order of $\pm$ 0.01 mg of free carbon. Thus, even for a free carbon content of the order of 0.1 mg the mean error amounts to $\pm$ 10%.

Example. A mixture of carbide plus excess carbon was taken. The total carbon found was 5.28 $\pm$ 0.11%

The results obtained for the determination of free carbon are adduced in Table 2.

TABLE 2

Experiment No.	Weight of carbide taken, in mg	Amount of free carbon found		Amount of free carbon corresponding to a mean of 0.26%, in mg	Δ_{free} - difference between C in columns (3) and (5), in mg
		in mg	in %		
1	2	3	4	5	6
1	42.5	0.114	0.27	0.111	-0.003
2	41.1	0.119	0.29	0.107	-0.012
3	40.8	0.089	0.22	0.106	+0.017
		Mean	0.26 $\pm$ 0.02%	Mean	+ 0.011

The results given in Table 2 show that the percentage error in the example given does not exceed $\pm \frac{0.011 \cdot 100}{42.5} = 0.02\%$ of the weight of the carbide and $\frac{0.011 \cdot 100}{2.5}$ of the weight of total carbon.

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1) See Consultants Bureau Translation, p. 405 (this issue).

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AN APPARATUS FOR THE QUANTITATIVE ABSORPTION OF GASES

B.F. Ormont and V.I. Smirnova

We have constructed a scrubbing apparatus of the types shown in Figs. 1 and 2 by means of which gases can be absorbed completely in solution and the solution subsequently used for gravimetric or volumetric determination of the gases.

The basic features of the scrubber are bells with gas outlets on top. The diameter of the opening is chosen in accordance with the experimental conditions. In the type used for CO_2 determination by absorption with barium hydroxide, the lower bells have an opening with a diameter of 2-3 mm while the diameter of the upper opening is 1-2 mm.

The apparatus shown in Fig.1 consists of individual bells fitted on to a tube which leads in the gas, and which itself ends up in a bell. Similar bells are mounted on top of each other ensuring good filling of the space between the plates (up to 10-12 bells in a length of 100-200 mm); the number of bells may be varied depending on the height h of the center tube.

The apparatus shown in Fig.2 is built on the same principle as that shown in Fig.1, but the tube on which the bells are mounted widens out in this case at its lower end and is filled with rings made from bits of thin glass tubing. This type scrubber has a number of advantages. When the gas is passing through, a large part of the solution is forced out by the gas from the inside and consequently even when small amounts of liquid are used the same effective height as that obtained with the apparatus shown in Fig.1 can be attained. The part of the solution left in the rings also participates actively in gas absorption. When absorption is carried out in this type of apparatus it is possible from time to time to stop the input of gas into the scrubber for an instand to create a higher pressure on the outlet side. This means that gas can proceed into the inside of the scrubber and leads to repeated soakings of the rings with solution. If any precipitate should form it falls onto the bottom of the scrubber through the wide openings into the lower part of the inner tube. In such cases, the lower bell should be at a distance of 15-25 mm from the bottom of the scrubber, which is sufficient for accommodating the precipitate.

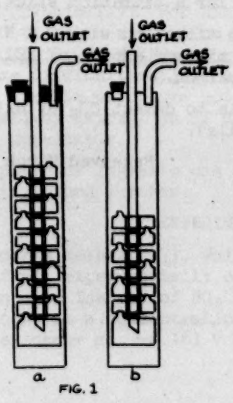

FIG. 1

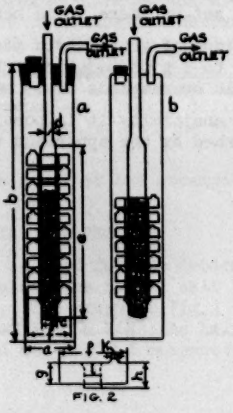

FIG. 2

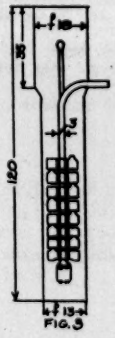

FIG. 3

Fig.1 Scrubber of the 1st type.

Fig. 2. Scrubber of the 2nd type. Number of plates, 10-12; g = 8-10 mm; h = 9-10 mm; i = C + 2 mm; k = 2-3 mm for lower and 1-2 mm for upper plates.

Fig. 3. Scrubber for microgravimetric analysis.

These scrubbers operate on the principle that the gas in broken up into small bubbles which are in contact with the absorbent solution for a long time. In some cases, e.g. absorption of CO_2 with barium hydroxide, a foam is formed which accumulates under the bells and to some extent on the surface of the solution; this also favors absorption.

Mixing of the solution by the gas passing through is very thorough even for a low overall gas throughput. This is a result of the fact that some of the gas has to accumulate on the plate before it can go through the openings.

For scrubbers of the type shown in Fig.2 which are used for CO_2 titration, standard sizes are given (in mms, see Table).

The tube leading into the scrubber may be fused in at its top end (Fig.1b, and Fig. 2b) or fitted with a rubber bung (Fig.1a, and 2a).

Of course, the gas could also be led into the bottom of the flask under the bells arranged on top of each other.

TABLE

Scrubber No.	a	b	c	d	e	f	h	V in ml
1	20/18	150	10/9	6/5	80	17/16	9	10-12
2	27/35	200	14/12	7/6	120	20/20	10	30
3	31/28	250	16/14	7/6	140	24/22	12	50

Note. The fraction sign denotes the outer and inner diameters, respectively, e.g. 20/18 means outer diameter 20 mm and inner diameter 18 mm. The volume of absorbent solution is given in ml (V).

For ultra-micro gravimetric titrations the apparatus is modified; the dimensions of the apparatus are much smaller (Fig.3), the total volume up to the top of the last plate is not greater than 4-5 ml; the top part is widened out so that the gas can leave more easily and a buret tip can be introduced. A glass rod with a sphere on one end is fused internally into the gas tube leading in the gas. By touching this rod with the buret tip a drop of any size can be taken off. The part of the drop falling on the rod remains inside the scrubber, and does not spread on the vessel walls and to other parts of the apparatus. In such a set-up there is no need for a titration stick.

Using the technique of gravimetric micro titration with 0.1 N HCl from a buret containing up to 1 g of solution, the minimum amount of HCl that can be taken is 10 mg which corresponds to 6γ of carbon.

With such high sensitivity it is possible to detect CO_2 of extraneous origin (e.g. CO_2 desorbed by the apparatus walls).

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POLAROGRAPHIC DETERMINATION OF NITRATES AND NITRITES IN SALTS AND BRINES USED FOR MEAT PICKLING.

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Heyrovsky and Nejedly [1], were the first to study the polarography of nitrites; they found that they are not reduced in neutral and alkaline electrolytes. Only after acidification of the solution did they find a wave at $E^{1}/_{2} = -0.77$ V (with respect to the normal calomel electrode), which was characteristic of the reduction of nitric oxide, and which permitted determination of nitrite down to concentrations of 10^{-5}N. Heyrovsky and Nejedly concluded that five electrons are involved in the reduction of NO, and that ammonia is the reduction product.

Subsequently Prat [2], Ruzicka [3], Tokuoka [4,5], and Tokuoka and Ruzicka [6], studied nitrates and nitrites polarographically. When LiCl or tetramethylammonium chloride were used as supporting electrolytes, respectively, reduction of NO_3^- and NO_2^- ions was observed at much more negative potentials. On adding multivalent cations (activators) to the test solution, displacement of the reduction potentials for nitrates and nitrites to more positive values was observed. Tokuoka and Ruzicka established that the diffusion current for nitrates and nitrites depends on the concentration of lanthanum chloride. Quantitative determination of NO_3^- and NO_2^- is possible when the $LaCl_3$ concentration is 50 times that of nitrate or nitrite; after improvements by other authors [7-12], this method was used for various practical purposes [13-16].

A new method of getting a wave for nitrate ions is to take polarograms in the presence of traces of uranyl salts. This method was proposed by Kolthoff and coworkers [17]. The "uranyl" method, which has since been used by other authors [18], for the determination of nitrites, has many advantages over the "lanthanum" method. Masek [19], on the basis of his critical examination of the problem, proposed that the lanthanum method, which is widely used in industry, be rejected, and that nitrates and nitrites be determined polarographically by the uranyl method.

Ingram [14], attempted to determine nitrates and nitrites in pickling brine polarographically. For nitrate determination he used a brine solution diluted 1000 times in a solution of 0.1 M $CeCl_3$ to which was added a mixture of 0.1 M $CeCl_3$, 0.001 M KNO_3 as standard. Working with Ce^{3+} salts however presents some difficulties; just as with La^{3+}, the polarographic waves for nitrate and nitrite, which are not themselves clearly defined, fuse into the current caused by deposition of alkali metals, and the results obtained are accordingly unreliable.

This paper of Ingram's was the basis of our attempt to develop the polarographic method further.

EXPERIMENTAL AND RESULTS

Kolthoff's method [17], which is used for the determination of nitrates was first of all experimentally checked; the normal salt $UO_2(CH_3COO)_2.2H_2O$, however, was used instead of UO_2Cl_2. The graph in Fig.1 shows the two waves for uranyl ions at a concentration of 10^{-3} M UO_2^{2+}; the half wave potentials of the two waves occur at -0.181 V and at -0.909 V respectively.[1]

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[1] All potentials are referred to the saturated calomel electrode.

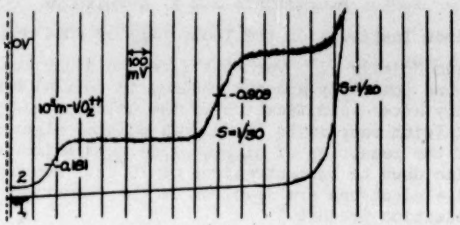

Fig.1

Uranyl Waves. Curve 1 - was taken with 4.5 ml of a solution of 10^{-1} M KCl 10^{-2} M HCl; starting at 0 V and with a sensitivity of 1/20. Curve 2 was taken with the same solution but 0.5 ml of aqueous uranyl acetate was added; the sensitivity in this instance was 1/30. A Kalousk cell with a saturated calomel electrode was used in a nitrogen atmosphere, the voltage being supplied from a 2V accumulator.

It was found that in the solution of 10^{-1} M KCl, 10^{-2} M HCl, $2 \cdot 10^{-4}$ M $UO_2(CH_3COO)_2$ on addition of nitrates in a concentration of $1.90 \cdot 10^{-5}$ to $1.38 \cdot 10^{-3}$ M KNO_3 there was an increase in the polarographic wave at -0.9 V. On increasing the nitrate concentration, its half-wave potential was shifted to more negative values. For the range of concentration just given these shifts amounted to -0.9 to -1.1 V (Fig.2).

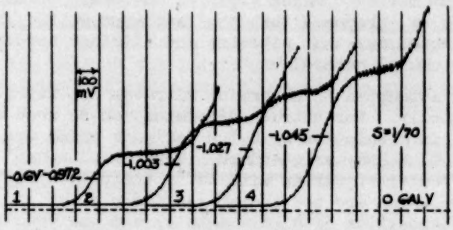

Fig.2

The Linear Relation between Limiting Current and Nitrate Concentration. To 5 ml of the supporting electrolyte 10^{-1} M KCl, 10^{-2} M HCl, $2 \cdot 10^{-4}$ M $UO_2(CH_3COO)_2$ was added some more of the same solution (0.1-0.4 ml) but containing 10^{-2} M KNO_3; in addition polarograms were taken starting from -0.6 V. The NO_3^- concentration for each curve was: 1 - 1.90; 2 - 3.80; 3 - 5.70; 4 - $7.40 \cdot 10^{-4}$ M KNO_3. The cell used was the Kalousk type with a saturated calomel electrode; electrolysis was carried out in a nitrogen atmosphere using a 2V accumulator as voltage supply and a sensitivity of 1/70.

Nitrites were studied in the same way. Using the same base electrolyte, they were found to be reduced at the potential of the second uranyl wave. The half-wave potential of the first uranyl wave was measured in a solution of 10^{-1} M KCl, 10^{-2} M HCl, $2 \cdot 10^{-4}$ M $UO_2(CH_3COO)_2$, 10^{-4} M KNO_2, and was found to be -0.181 V, while the potential of the second uranyl wave which coincided with that of the nitrite ions was found to be -1.018 V. Using the same base

electrolyte but at higher concentrations of KNO_2 of $1 \cdot 10^{-4}$ to $7.47 \cdot 10^{-4}$ M KNO_2, the more negative wave increased linearly with increasing nitrite concentration, but its half-wave potential remained practically constant in contrast to that for the nitrates.

These experiments demonstrate the advantages of the uranyl method which requires insignificant amounts of uranyl acetate over the lanthanum or cerium methods.

Determination of Nitrates in Pickling Salt

Pickling salts do not contain organic additives (in contrast to salts use for rapid pickling) and should contain, according to State standards [28] only sodium chloride plus 2.00 - 3.70% of potassium nitrate. These mixtures are prepared in refrigerators by mixing the components and the permitted amounts of KNO_3 is not always observed. Apart from the poisonousness of the nitrate itself, there is a possibility of the formation of the even more poisonous nitrites in impermissible amounts during pickling by the action of micro-organisms. It is essential therefore to control the nitrate content both in the solid mixtures used for meat pickling, and in the pickling brine. The uranyl method can be used for nitrate determination in these cases. The supporting electrolyte is 10^{-1} M KCl, 10^{-2} M HCl, $2 \cdot 10^{-4}$ $UO_2(CH_3COO)_2$[1]; to this is added a similar solution which in addition contains 10^{-3} M KNO_3 (Fig. 2), and a calbration curve drawn, the wave height at - 1 V is measured. A 1% solution[2] of pickling salt is then prepared in the above supporting electrolyte and a polarogram taken. Having measured the wave height at - 1 V, the KNO_3 concentration is determined from the calibration curve. If the nitrate content of pickling brine (10 - 25% aqueous solutions of pickling salt) is required, then the brine is diluted 10 times and further additions of standard solution and supporting electrolyte added so that the final concentration of the test solution will be 10^{-2} M with respect to HCl and $2 \cdot 10^{-4}$ M with respect to uranyl acetate.

Determination of Nitrite in Salt for Rapid Pickling

"Praganda"

In view of the poisonousness of nitrites it is necessary to ensure a strict control over the nitrites used for rapid pickling, in which the maximum and minimum amounts of sodium nitrite should be 0.6 and 0.5%, respectively. No nitrates can be added to these salts under any circumstances [20, 21].

The uranyl method cannot be used for exact polarographic determination of nitrites in this type of pickling salt (i.e. salts for rapid pickling). The reason for this inapplicability of the uranyl method is the poor reproducibility of the linear relation between concentration of nitrate and height of the nitrite wave, because of the formation of two unknown waves, apparently resulting from the presence of sugars or starches in the pickling salt [23-27].

It was found however that by carrying out the electrolysis in an acetic acid medium the reproducibility of the polarographic wave was good; on passing an inert gas through the solution the wave disappeared completely, thereby showing that it is the result of the reduction of nitric oxide (Fig. 3).

The Nitric Oxide Wave in "Praganda". Curve 1 - 1 ml of 96% acetic acid was added to 9 ml of a 11.1% aqueous solution of "Praganda" after passing nitrogen through the solution; when the resultant solution had been mixed with a glass rod a polarogram was taken starting at 0 V. Curve 2 - The same final solution as for Curve 1 after passing nitrogen through for a short time.

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1) The $2 \cdot 10^{-4}$ M solution contains 0.848 g $UO_2(CH_3COO)\ 2H_2O$/liter.

2) The required weighed amount of "Praganda" (a particular type of pickling salt) is taken from a solution of known concentration, the latter being prepared by dissolving at least 10 g of sample.

Curve 3 – the same after passing nitrogen through for a fairly long time. A Kalousk cell was used in conjunction with a saturated calomel electrode, nitrogen was used for sweeping. a 2 V accumulator supplied the voltage and the sensitivity was 1/200.

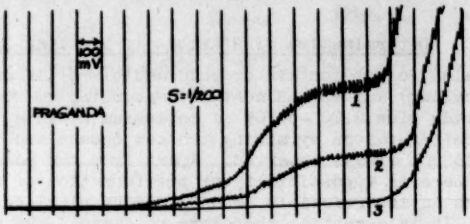

Fig. 3

The following simple method can accordingly be recommended for the polarographic determination of nitrite in salts used for rapid pickling, such as "Praganda".

Solutions. 1) A 10% solution of "Praganda" free from atmospheric oxygen (10 g of solid salt is dissolved in distilled water and made up to 100 ml, the oxygen is expelled beforehand by bubbling nitrogen through it); 2) a standard aqueous solution of 10^{-2} M $NaNO_2$ free from atmospheric oxygen; 3) 10% acetic acid.

Analytical Procedure. 9 ml of 10% acetic acid solution is placed in an electrolytic cell and nitrogen blown through. 1 ml of the 10% solution of "Praganda" free from atmospheric oxygen is then added and the mixture carefully mixed (with a glass rod). Polarograms are taken starting from −0.6 V, using a 2 V accumulator and a sensitivity of ca. 1/100 - 1/500. After recording the curve, ca. 0.5 ml of standard nitrite solution also free from atmospheric oxygen is added, the solution mixed again, and another polarogram taken.

Notes. If nitrites are to be determined in white brine used for rapid pickling (ca. 10 – 20% solution of "Praganda") then the solution can either be placed directly in the electrolytic cell or preliminarily diluted with distilled water free from atmospheric oxygen. Electrolysis is carried out in an inert gas atmosphere, and the mixture carefully mixed after addition of the nitrite so as not to expel the readily volatile nitric oxide. For a large number of determinations the use of a calibration curve is more expedient, while for single determinations the method of standard additions may be used.

An example of how to calculate results from a polarogram when the method of standard additions is used. A standard solution was prepared from 0.0851 g of solid 91.29% $NaNO_2$. Calculated on a basis of 100% $NaNO_2$ this is equivalent to 0.0776 g of $NaNO_2$. This amount was dissolved in distilled water free from oxygen, and the solution diluted to 100 ml. The solution was then 0.0112 M with respect to $NaNO_2$, and 0.5 ml of the solution contained $3.88 \cdot 10^{-4}$ g $NaNO_2$. Calculationn is made by means of the formula

$$x = \frac{hmV}{h'(V + a) - hV},$$

where x – is the amount of $NaNO_2$ in g contained in 1 ml of the 10% solution of "Praganda"; h – 29 mm (the height of the wave for weight x of $NaNO_2$; h' – 45 mm (the height of the wave after addition of standard) V – 10 ml

(the volume of the solution being electrolyzed before addition of standard); $\underline{a}$ – 0.5 ml (the volume of standard added); $\underline{m}$ – $3.88 \cdot 10^{-4}$ g (the amount of $NaNO_2$ in g in the volume of standard added, $\underline{a}$).

Substituting these values in the formula we get $x = 0.616 \cdot 10^{-3}$ g $NaNO_2$. The test sample of "Praganda" therefore contains 0.62% sodium nitrite in the solid state.[1])

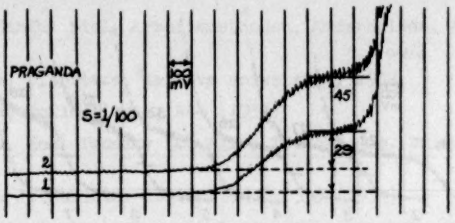

Fig. 4.

Determination of Nitrite in "Praganda".

Curve 1 – to 9 ml of a 10% acetic acid solution through which nitrogen had been passed was added 1 ml of a 10% aqueous solution of "Praganda" free from oxygen, and the solution polarographed, starting at 0 V.

Curve 2 – to the solution with which Curve 1 was taken was added 0.5 ml of 0.0112 M $NaNO_2$ solution free from oxygen. The solution was electrolyzed in a Kalousk cell using a 2 V accumulator and a sensitivity of 1/100; the reference electrode was the saturated calomel electrode.

Determination of Nitrates and Nitrites in Red Brine (Used Brine).

While it is only necessary to determine nitrates (in the brine made from pickling salt) or nitrites (in the brine made from salts used for rapid pickling) in fresh brines (the so called "white" brines, i.e., brines not previously used for pickling), in used brines (the so called red brines) it is necessary to determine both nitrates and nitrites simultaneously. In the course of only 20 days of pickling the salt is under the action of reducing denitrifying bacteria, so that nitrite is formed [20]. On the other hand, in fresh nitrite pickling salt a small amount of the nitrite is converted into nitrate and only after approximately 60 days of pickling do both these salts disappear from the pickling liquid as a result of decomposition by micro organisms and combination of free nitric oxide with hemoglobin to give nitrosohemoglobin [20].

The methods proposed in this article from the polarographic determination of the solid salts used for pickling and for preparing fresh brines are important from the point of view of preventing poisoning which may arise as a result of haphazard and irresponsible methods of preparing the salt mixtures. Determination of nitrates and nitrites in used brine allows one not only to control the pickling process but to regulate it subsequently.

During polarographic investigation of used brines it was shown that even on strong dilution the effect of proteins coming from the meat led to poor reproducibility of the calibration curves when the "uranyl" method was used. This drawback was overcome by precipitating the proteins with alcohol. To 1 ml of used mitrate solution was added 2 ml of ethyl alcohol and the solution left in a test tube on a water bath until most of the protein had been

1) Chemical analysis of "Praganda" by titration with $KMnO_4$ [22], also showed that this sample contains 0.62% sodium mitrite.

precipitated. The filtrate was diluted with distilled water to approximately 48 ml, 0.5 ml of $2 \cdot 10^{-2}$ M $UO_2(CH_3OO)_2$ was then added and the whole made up with more water to exactly 50 ml. When such a solution is used after adding the usual supporting uranyl electrolyte a linear relation is obtained between concentration and wave height at −1 V (Fig. 5), $E_{1/2}$ is normally shifted to more negative potentials.

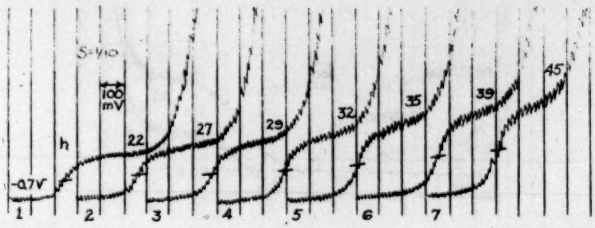

Fig. 5

Nitrate Waves in Used Brine. Curves 1 – 9 were obtained in a uranyl supporting electrolyte (10^{-1} M KCl, 10^{-2} M HCl, $2 \cdot 10^{-4}$ M $UO_2(CH_3COO)_2$; electrolysis was carried out in a nitrogen atmosphere.

Curves 2 – 7 represent what happens when to the solution used for taking Curve 1 was gradually added 0.2 ml lots (1.2 ml altogether) of the solution of used nitrate brine diluted 50 times and partially freed from protein by addition of alcohol; the final solution was $2 \cdot 10^{-4}$ M with respect to $UO_2(CH_3COO)_2$. Polarograms were taken from −0.7 V in a Kalousk cell with a saturated calomel electrode, the voltage was supplied by a 2 V accumulator, in N_2 and the sensitivity was 1/10.

No wave was evident on the polarogram for the brine at −0.7 V (partially freed from NO), consequently this brine did not yet contain nitrite formed by microbe action (this is in agreement with the age of the brine, since it had only been in use for 14 days), the wave at −1 V in Fig. 5 is caused by reduction of nitrates only.

For determining nitrate in brine previously used, electrolysis is carried out in acetic acid medium (as described for "Praganda"); acetic acid precipitates proteins so that there is no need to add alcohol.

After recording the NO wave at −0.7 V, inert gas is passed through the solution to free it from nitrites. Nitrates can then be determined by adding the usual uranyl supporting electrolyte and following the "uranyl" method.

The authors wish to thank the Directors of the Prague Meat Industry, and the " Khmel" factory for gifts of samples of pickling salts and to A. Funfalk of the " Praganda" factory for his valuable discussion of results.

SUMMARY

The authors have tried to modify the polarographic method used for determining nitrates and nitrites in meat pickling salts.

The uranyl method is recommended for analysis of nitrates in pickling salts. In red pickling salts it is necessary to remove protein beforehand by precipitation with alcohol on a water bath. In the case of salts used for rapid pickling the authors determined nitrite in an acetic acid medium on the basis of reduction of the freed nitric oxide. Because of the presence of various organic contaminants (e.g. sugars, starches, etc.) which are added to

the salts for rapid pickling, this determination can be recommended as being a more accurate method than the $KMnO_4$ method.

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A STUDY OF THE ERRORS INVOLVED IN THE CHEMICAL ANALYSIS OF STEELS AND CASTS

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Correct evaluation of the errors of chemical analysis is one of the most important factors which decide further improvements in the quality of analytical work. Such an evaluation is only possible by sorting out random from systematic errors of chemical analysis and finding out the contribution of each to the total error. Unfortunately, the importance of this point is underestimated. We aimed at finding out what is the individual importance of systematic and random errors in the errors of chemical analysis, reckoning that if we succeeded then our findings could be used as a basis for recommending improvements.

The most complete information re the evaluation of errors in chemical analysis is obtainable from the results of a large number of analyses carried out in the most highly qualified laboratories. Of interest from this point of view is the material from the archives of the laboratory of Standard Samples (LSO).

Let us consider briefly what information a study of this material can give us. Investigations of this type should embrace the study of the scattering of results in a series of measurements - by a study of random errors - by comparing the results of analysis of samples with reliable data on the composition of these samples (i.e. by comparison with standards) - and by studying systematic errors. In general, carrying out such an investigation presupposes realization of three conditions: 1) in studying random errors the treated results should actually represent statistically random values; 2) in studying systematic errors the results should not be distorted by superposition of random errors; 3) chemical standards should be available if any decision is to be made as to the existence of systematic errors and as to their size. In practice all these conditions are not completely fulfilled.

Experience has shown that results of chemical analysis of the composition of standard samples and of spectrographic standards cannot be regarded as statistically random and independent, in particular, on account of the fact that the statistical randomness of the results is distorted by the compulsory rejection of some of the results during the process of establishing the chemical composition. It is true to say therefore that the actual scatter of results exceeds that which can be calculated from the material available in the analytical archives.

The second condition, although it can only be satisfied to a limited extent, nevertheless can be satisfied to an extent sufficient to ensure good enough accuracy when special methods of calculation are employed.

If the third condition is to be fulfilled, then, strictly speaking, it is essential to know the true composition of the test material, this is of course impossible. One must, therefore, replace comparison with standards the results of which are known to be reasonably accurate, by a comparison with standards the composition of which are only known to various degrees of approximation. As an arbitrary standard, for want of a better one, it is possible to use the mean content of an element in a standard sample (or spectrographic standard) as established from the results of all the analysts.

Thus, the values of random and systematic errors of chemical analysis, which are obtained by treating test material similar to that of the analytical archives of the Laboratory of Standard Samples, should be considered as values established with a definite approximation.

An attempt to treat such material was made by Groshev and Ponosov [1]. These authors assumed that in chemical analysis there exist some systematic errors which do change under any circumstances but are innate in the method itself (method error), and systematic errors which are innate in a given series of measurements and which arise as a result of factors unrelated to the nature of the method. In their investigations only method errors were studied, so that they did not give a complete picture of the value of systematic errors. Practice shows that results of analysis carried out in different laboratories even when the same method is used, often exhibit a systematic deviation. This testifies to the important part played by systematic errors which are not related to the nature of the method. It is therefore more correct to use the term systematic analytical error in the sense of a constant error inherent in a given series of measurements of chemical composition carried out by an analyst or laboratory, and not only in the sense of an "error in method" or a "constant value" as if it were a characteristic of a given analyst or laboratory in general, irrespective of the test material analyzed.

In preparing the original results for calculation the authors of the article indicated [1], evaluated the compatibility (as a member of one statistical series) or incompatibility of the measurements of two analysts by the Student-Fisher Test [2], in which they exclude obviously incompatible results, and assumed that the difference in the averages compared in the remaining instances was random assumed united into one statistical series. Nevertheless a large number of measurements not excluded by these authors could contain values which very often vary to a considerable extent, in addition to the random and systematic errors which are inherent in one or another group of results, although it would be impossible to establish these reliably because of the significant uncertainty in the values found for the dispersion when dealing with a small number of measurements (4-6 for each of the dispersions compared in evaluating the compatibility of the measurements made by two analysts; 8-12 for evaluating the measurements of two laboratories). Moreover the case is possible where both sets of measurements being compared have a common systematic error.

We carried out a statistical treatment of material available in the analytical archives of the LSO, in which we took into account the deficiencies of the previous work (some of the original material used for calculation and obtained by the authors of [1] was used for this purpose). Material obtained on the analysis of standard samples and spectrographic standards for simple and multi-component steels and casts were treated.

The following method of calculation was used for determining the value of the random errors in chemical analysis. In order to eliminate the effect of hidden systematic errors, the dispersions were calculated from the results obtained by each analyst separately, and not from all the mass of material taken as a whole. Each of the values found in the way for the dispersion σ_i^2 as a result of treating a small number of measurements was not reliable enough. Nevertheless the mean value of the dispersion

$$\sigma^2_{av.} = \frac{\sum \sigma_i^2}{n}$$

where n – the number of analysts participating in the analysis of a given standard sample or spectrographic standard (usually 16-20), characterizes the accuracy of the determination considerably more reliably. By using this technique it is possible to exclude not only the effect of hidden systematic errors inherent in the results of various laboratories but also to exclude the effect of hidden systematic errors inherent in the results of different analysts

even though working in the same laboratory. Using the mean values found for the dispersion, calculations were made of the corresponding mean square errors which were expressed in relative percentages (in all 6000 measurements were dealt with). The relations established between the values determined for the contents of various elements and the value of the mean square errors are adduced in Fig. 1.[1)]

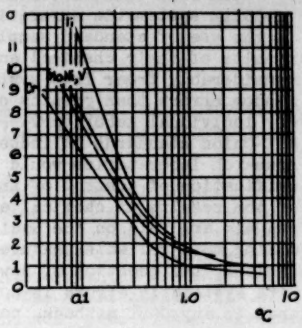

Fig. 1. Change in value of the random error (mean square error of a "single measurement") of chemical analysis of steels and casts with the value of the content of the element determined (the value of the error is expressed in relative %).

Evaluation of the systematic errors of chemical analysis is incomparably more difficult since the true contents of the test elements are unknown. If, arbitrarily, in the absence of information as to the true composition, one should start off with the average content established from the mean results of all the analysts for a given standard sample or spectrographic standard, then one can take the deviation of the mean results for each laboratory (mean of 8-10 determinations by each method) from the calculated overall mean as the value of the systematic error.

The relation between the systematic errors calculated in this way and the value of the contents determined for the elements is adduced in Fig. 2. (results of treating ca. 1200 means). It is pertinent to point out that the curves adduced in Figs. 1 and 2 reflect only the mean values of the errors, while at the same time one very often comes up against considerable deviations from the means.

The results adduced show that the values of the systematic and random errors are of the same order, even when carrying out such responsible work as the chemical analysis of standard and spectrographic standards.

When measuring the results of several meansurements, if the value of the random error of a result decreases then the specific contribution of the systematic errors correspondingly increases. This is observed in particular also when comparing the results of several laboratories determining the composition of standard samples and spectrographic standards: in many cases the results of each laboratory are grouped round its mean, but the mean, despite averaging, still differs from one laboratory to the other.

When, in addition to what has already been said, one takes into account that metrological requirements for the exclusion of systematic errors are incomparably more strict than for random errors [3], then it is true to say that the question of controlling systematic errors has a significance for analytical practice which is at least as great, if not of greater, importance than the question of controlling random errors.

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1) The curves given in Figs. 1 and 2 were constructed from results obtained for all the methods of chemical analysis employed, since it had not been established that any particular method gave any essential different accuracy or reliability from other methods used for the chemical analysis of standard samples or spectrographic standards.

The sole effective means of controlling systematic errors in analysis is the use of standard samples since the results of their chemical analysis are considerably freer from systematic and random errors than results obtained in any individual laboratory. The use of All-Union standards in industrial and research laboratories would signify the unification of control of the correctness of the results of chemical and spectrographic analysis on the basis of introducing more reliable measures. Nevertheless, the question of how to deal with systematic errors is not touched upon in any GOST methods, nor has the use of standard samples and spectrographic standards for the control of analytical results been specified. Meanwhile, the results obtained do show that in considering the question of analytical errors proper attention must be paid not only to the evaluation and control of random error but also to the evaluation and control of systematic errors. Such an evaluation and control should be carried out by analyzing standard samples and spectrographic standards similar in composition and properties to the test sample. When this is done it is essential to ensure the necessary accuracy of the test results obtained (to eliminate random errors). The permitted values of the deviation of the mean result obtained from the certified results of the standard samples and spectrographic standards should be established, taking into account the acceptable values of the systematic errors and the accuracy of the mean results obtained.

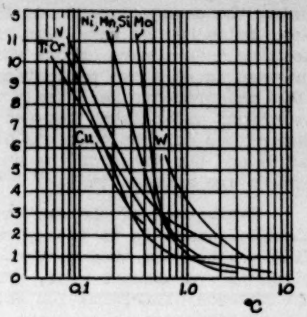

Fig.2. Change in the value of the systematic error in the chemical analysis of steels and casts with the value of the determined content of the elements (the value of the error is expressed in relative percentages.)

SUMMARY

Systematic and random errors arising during chemical analyses of standard samples and spectrographic standards of steels and casts have been studied separately. It has been shown that the systematic errors which arise during chemical analysis are of the same order of magnitude as random errors of single measurements and exceed the random errors of results obtained by averaging several measurements. In this connection the importance of using All-Union standard samples for controlling systematic errors is emphasized.

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CRITICISM

A. I. Busev. The Analytical Chemistry of Bismuth. Acad. Sci. USSR press, Moscow, 1953, pp. 382, 100 Tables containing numerical data. Bibliography of 1396 references. Printing 2000. Price 21 rubles.

A.I. Busev's book is the first monograph in Soviet chemical literature to be devoted to an overall survey and critical exposition of the method used for detecting and determining bismuth in its compounds and in products of various origins. The most worthy feature of the book is the clear and logical way it is set out. The author divides his book into seven chapters which are based on the types of reactions characteristic of bismuth ions. The first chapter is devoted to the hydrolysis reactions of bismuth compounds; some of the reactions were already known during the XVI century. The practical use of these hydrolysis reactions for qualitative and quantitative analyses relates to the beginning of the last century. Further improvements were made to hydrolysis methods recently. Instead of water, alkali hydroxides, or carbonates, which were used in the past, the tendency now is to use materials exhibiting buffer action for hydrolyzing bismuth salts materials such as: urotropine, pyridine, sodium formate, sodium nitrite, ammonium carborate, etc. The basic bismuth salts which are formed on hydrolysis such as BiOCl, BiOBr and $(BiO)_2CO_3$, can be used for the gravimetric determination of this element. The accuracy of methods based on hyrolysis is not very good, but is nevertheless good enough for technical analysis of ores, alloys, and also of pharmaceuticals.

The methods proposed by P. P. Solodovnikov are successful examples of these methods. The method of coprecipitation developed by N.A. Tananaev and coworkers is of special importance for the separation of bismuth from other heavy metals and for the detection of bismuth.

The author of this book has paid little attention to preventing hydrolysis of bismuth salt solutions. This problem which is not only of analytical importance but also of biological significance has been studied by Turkevich [1]. New light has been thrown on the composition of bismuth tartrate complexes in the published papers of Tsimbler [2], and Tikhonov [3].

In the following chapter the reactions of bismuth with inorganic anions are discussed. Most gravimetric determinations of bismuth are based on the formation of the sulfide, phosphate, arsenite, bichromate, hexathiocyanochromate, and other sparingly soluble compounds of this metal. The detailed study of the properties of bismuth sulfide is of special importance. Determination of the solubility product carried out by A.F. Kapustinsky, and also the position occupied in the solubility series of the metal sulfides, as pointed out by N.A. Tananaev, permit one to forecast the behavior of bismuth ions during analysis.

The formation of the acid-stable phosphate $BiPO_4$ is used at present not only for the analysis of bismuth but also for the determination of phosphoric acid.

Valuable information is given in this section on the determination of bismuth in its organic compounds, and also in biologically important materials.

The separation of bismuth from the other metals of the hydrogen sulfide group, such as mercury, lead, thallium, cannot be regarded as fully worked out. A careful study of the physico-chemical reaction conditions will undoubtedly lead to further improvements in these difficult determinations.

The next chapter deals with the reactions which occur between bismuth and organic molecules. The use of organic reagents in analytical chemistry, which

was proposed at the beginning of this century by L.A. Chugaev, is of great importance also for bismuth. The thiourea complexes of bismuth, which have been known for 50 years, find application for the qualitative detection and colorimetric determination of this metal.

A number of sulfur-containing compounds are used in the analytical chemistry of bismuth, among these are; diphenylthiocarbazide, dithizone, captax, thionalide, and many others. Thionalide still remains the most convenient reagent for detection and determination of bismuth. The use of dithizone ensures high sensitivity. The worst feature of this method is the necessity of using CCl_4 or $CHCl_3$ as solvents.

Phenols constitute the second large group of organic compounds which give characteristic compounds with Bi^{3+} ions; among these mention should be made of pyrogallol, gallic acid, and also oxine.

Complexone III (Trilon B) has very recently been suggested for determination of bismuth; the sodium salt of ethylenediaminetetracetic acid in the presence of a special indicator -pyrocatechinsulfonphthalein - this method has been suggested in the works of Malat, Suk, and Ryba [4].

The fourth chapter of the monograph deals with all the numerous complex halides of bismuth which usually contain organic bases as well. The iodide derivatives of bismuth which contain the ions: $[BiI_4]^-$, $[BiI_5]^{2-}$, $[BiI_6]^{3-}$, $[Bi_2OI_8]^{3-}$, etc., are of utmost importance in analytical practice.

In the case of complex bases the iodo- bismuth reactions are not so much used for the detection of bismuth as for the identification of the base or alkaloid itself. Reactions with quinine, cinchonine, brucine, caffeine, cocaine, strychnine, narceine, and other alkaloids, which were first studied by Dragendorf [5], are of this type.

The thiocyanate complexes of bismuth are similar in character to the halides. Thanks to the work of the Yu.Yu. Lurye, A.K. Babko, and I.M. Korenman, colorimetric methods have been developed for bismuth with sensitivities down to 0.1 γ/ml.

The subsequent section of the book is devoted to reactions which occur at high temperatures, chiefly in the dry state. The title heading: "Some reactions which occur without a change in the valency of bismuth" does not really demonstrate what the reactions have in common.

The behavior of bismuth oxide and bismuth sulfide at high temperatures, and also results on the volatility of the bismuth halides, are of exceptional importance for the analytical determination of this element. This is confirmed by the work of the French chemists Panchout and Duval [6], which was published after the present book was written; their paper "Thermogravity of organic precipitates" No. XLVII contains results on 36 bismuth compounds. Busev should expand this chapter in future editions.

Oxidation-reduction reactions of bismuth compounds are considered in chapter 6. Reduction of bismuth to metal by means of various reducing agents is the most important in this connection.

Exceptionally good results were obtained by Busev when he used chromium dichloride as reducing agent. $TiCl_3$, $SnCl_2$, $VOSO_4$, H_3PO_2, $Na_2S_2O_4$-etc. have been successfully used in acid media. Reduction reactions can also be carried out in alkaline media by using sodium stannite, formaldehyde, glucose, and complex manganese and nickel cyanides as reducing agents. Replacement of bismuth electrochemically by other metals is also used. Of interest from a theoretical point of view, although it has not been studied sufficiently, is the reaction: $3Cu + 2Bi^{3+} \longrightarrow 2Bi + 3Cu^{2+}$, which follows different paths according to the presence of complexing ions, pH, and rH of the medium, and other experimental conditions. Oxidation of bismuth to higher valencies followed by reduction

is not quantitative and is therefore of little significance in analytical chemistry.

The last chapter is devoted to physico-chemical methods of detecting and determining bismuth. This chapter includes brief reviews of the following methods: flame coloration, quantitative spectrographic analysis, X-ray analysis, and also the marked atoms method. A. Busev's review in Progress of Chemistry, [7] leads us to suggest that the author should supplement this section of his outstanding monograph.

The bibliography is exceptionally well worked out and embraces 1396 references, covering the period from the beginning of the last century to 1951.

One of the drawbacks of the book is the absence of an author index, so that one cannot look up papers by a particular author in the text. The few mistakes in the book do not lower the overall importance of this book as a contribution not only to Soviet but to world chemical literature.

The success of this monograph on the analytical chemistry of bismuth should serve as an impetus for extending this idea to other elements.

Lvov

August 31, 1954

K.N. Mikhalevich
N.M. Turkevich
L.I. Panteleeva

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DMITRII IVANOVICH RYABCHIKOV

(On his fiftieth birthday)

On the 6th of November Dmitri Ivanovich Ryabchikov, one of our foremost chemists - a doctor of chemical sciences, a professor, and a Stalin prize winner - celebrated his 50th birthday.

Dmitri Ivanovich, a pupil of N.S. Kurnakov, is well known as a scientist fruitfully working in the fields of theoretical and practical inorganic and analytical chemistry on problems connected with the study and analysis of the rare and noble metals.

Ryabchikov finished in the Technical Department of the Plekhanov Moscow Institute of Natural Economy in 1931.

After finishing in the Institute he became a candidate for a degree in the Institute of General and Inorganic Chemistry, Acad. Sci., USSR, and in 1934 defended his thesis on the "Strength of Isomeric Bases" which he carried out under the direction of Corresponding Member of the Academy of Sciences A.A. Greenberg.

While a coworker at the Institute of General and Inorganic Chemistry Ryabchikov headed a number of expeditions to study salt deposits.

Under the direction of Academician N.S. Kurnakov he studied the potassium-magnesium deposits of the sulfate type in various parts of the Soviet Union. He showed that certain minerals contained potassium. He also demonstrated the high efficiency possible by using mixed potassium sulfates as fertilizers.

He also carried out work on the stereochemistry and physical chemistry of noble metal complex compounds. He was the first to characterize the large class of the thiosulfate compounds of platinum, palladium, silver, gold, and of other elements.

Many of the complex compounds which he synthesized (over 50) contained a complex ion with six charges, which is something new in the chemistry of complex compounds. The thiosulfate compounds are more stable than any hitherto known.

The thiosulfate "Ryabchikov reaction" is one of the most reliable means of determining the isomeric character of complex compounds. He also carried out work on the stereochemistry of complex compounds along other lines, in particular, he prepared and characterized the little-studied class of the sulfite complex compounds (e.g. $Na_2[Pt(SO_3)_2(NH_3)_2]$, $Na[Pt(Tham)_2\ (SO_3)_2]$, etc. He showed that SO_3^{2-} is a vigorous complexing agent and is comparable with thiosulfate and thiourea.

Ryabchikov was the first to establish that in complex compounds there is a relation between strength and isomeric character. Of exceptional importance is the work he did on the application of electrometric titration for solving a number of problems connected with a study of the structure of the inner sphere of complex compounds.

His work on the mechanism of oxidation of platinum thiosulfate compounds by potassium bromate, in which he used potentiometric titration, is very interesting. This method permits determination of the instability constants of many complex platinum compounds, and on the basis of the results it is possible to solve the question of the polarization of complex molecular compounds.

By studying the thiosulfate compounds of silver – $Na_3[Ag(S_2O_3)_2]$, $Na_4[Ag_2(S_2O_3)_3]$ – he showed that silver can occur not only in the inner but also in the outer sphere of the complex, depending on the concentration of the reactants, e.g. $AgNa_2[Ag(S_2O_3)_2]$.

These researches on the thiosulfate compounds of platinum and other metals were made the basis of his thesis for his doctorate, which he defended in 1942.

The development of theoretical studies on complex compounds served as a basis for working out analytical methods. Potentiometric and colorimetric methods were particularly widely used.

In the analytical chemistry of the platinum metals (Pt, Ir, Rh, Os and Au) Ryabchikov developed original methods of detecting individual metals and analyzing alloys, and industrial intermediates. These methods are used in control work; e.g. cerimetric determination of lead, or the colorimetric determination of rhodium in the presence of platinum, etc.

Ryabchikov has been devoting his time recently to the elements of the rare-earth group. In this hitherto little-studied branch of inorganic chemistry he has successfully applied the teachings of the Chugaev school.

New complex compounds of elements of this groups have been isolated by Ryabchikov. It has been established that these elements are specific complexing agents which differ essentially from many other heavy elements. Being quadrivalent they have a coordination number of "six". Rare-earth ions do not form non-ionic bonds with the majority of the usual coordinating substituents, even such vigorous ones as the thiosulfate, iodate and nitrite ions etc; on the other hand, organic amines which contain a tertiary nitrogen form complex compounds of average stability.

The coordination bond in this group of metals is best formed through an oxygen atom to carbonates, sulfates and other inorganic acids, and particularly with organic acids containing a few carboxyl groups. A vast amount of information has been collected on complex formation between rare earths and carboxylic acids, monobasic, dibasic, and tribasic hydroxy acids, mono- and multi-basic amino acids, and sulfonic acids of the benzene, naphthalene, and anthracene series. It has been established that the combination in an organic molecule of three carboxylic groups (nitrile, triacetates, citrates) ensures the formation of very stable complex ions.

Isomeric compounds of this type have been prepared, e.g. for praseodymium and neodymium; they alternately enter the inner and outer spheres.

One of the characteristic features of the complex compounds of the rare-earths is extreme sensitivity to change of medium; increasing the acidity of their solutions leads to weakening of the coordination bond and a switch to an ionic state.

The work being carried out in the laboratory of the Vernadsky Institute of Geochemistry and Analytical Chemistry under the direction of Ryabchikov on analysis, isolation, and preparation of the rare-earths from natural minerals by chemical and chromotographic methods is an essential contribution to the chemistry of the rare-earths.

A note may be given here of a new sensitive reaction and a colorimetric method for determination of cerium which are based on the formation of a citrate complex $Na_5[Ce(C_6H_5O_7)_3]$ with hydrogen peroxide in alkaline media.

During a study of the thiosulfate complexes of certain rare-earths, Ryabchikov isolated new compounds in alcoholic media and clarified the mechanism of interaction between quadrivalent cerium and thiosulfate.

Ryabchikov and his coworkers have made a concerted attack on the possibilities of using ion-exchange resins in analytical chemistry, in particular for the separation of rare-earths and some others, and also for the preparation of inorganic compounds in a very pure state.

The theory which he has developed re the chemical nature of ion exchange processes has found recognition among research workers in the field of chromatography, and has opened up ways of synthesizing resins with selective action. Under his direction a valuable comparative study of Russian synthetic ion-exchange resins has been made. Analytical methods involving the use of ion-exchange materials have been proposed, e.g. determination of copper and iron in alloys, in which differences in the stability of phosphate and ammonium complexes are used; determination of rhenium in molybdenum concentrates, etc.

All Ryabchikov's scientific activity has been indissolubly linked with teaching. For 20 years he has been teaching chemistry in the Moscow Region Teaching Institutes and has held the chair there. During his time he has taught numerous cadres of chemists in intermediate schools and his teaching experience has been incorporated in a text book of chemistry.

His research students work on the chemistry of the complex compounds of the rare-earths and on chromatographic analysis.

He is also in close touch with industrial and factory laboratories, and acts as a scientific consultant on various questions of production control.

His organizing activity as a deputy director of the Vernadsky Institute is also worthy of note, he has devoted much time and energy to developing the analytical section of this Institute. Being a deputy chairman of the Commission on Analytical Chemistry, he has striven to improve industrial production of chemical reagents and apparatus; in addition he has been instrumental in calling scientific conferences on analytical chemistry.

From its inception, Ryabchikov has been secretary to the board of "U. Anal. Chem." and also the editor of several papers and monographs.

The government value his services highly. He has been awarded a Stalin prize. He has also been awarded the orders of Lenin, and the Red Banner, and a Badge of Honor.

He is well liked and honored by a wide circle of analysts.

In celebrating his birthday his numerous pupils, coworkers and friends wish him the best of health, and hope that he will gain further successes in developing analytical chemistry for the benefit of our country.

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NINTH CONFERENCE ON SPECTROSCOPY

The 9th conference on spectroscopy which was held at Tartu in the Estonian Republic from the 5th to the 11th of July, was attended by 700 representatives of scientific research institutes, higher education establishments, and factories from various parts of the Soviet Union.

One hundred and eighty five papers were read at the conference, of which 53 were devoted to molecular spectroscopy, while the others were devoted to studies of atomic spectra, to processes occurring at the excitation source, spectrographic apparatus, and spectrographic methods of analyzing various products.

Fifteen reports were concerned with descriptions of new apparatus made in Russia and indicated considerable achievements in the production of spectrographic equipment.

The first spectrographs with diffraction gratings to be put into production were the flat (DSF-3) and curved (DFS-2) types. These instruments are distinguished by high linear dispersion – 2A/mm to 4A/mm (in the first order) and a high resolving power – 100,000-150,000. The diffraction gratings are modern and as good as foreign makes.

The three prism spectrograph, the ISP-67, with a resolving capacity of 150 000, is of the class which has a high dispersion; this instrument is also characterized by high candlepower, whereby the superfine structure of mercury can be observed. Two other spectrographs have also been issued: the ISP-66 (similar to the ISP-22) with a mirror collimator (parabolic mirror) which can be used for observing weak fluorescence; the super candle power spectrograph (ISP-63) which has large prisms is suitable for expedition conditions; with this instrument the illumination of the night sky can be investigated. Vacuum instruments of three types have been developed by our industry: 1) with a bent diffraction grating which permits spectra in the extreme ultraviolet to be obtained; 2) a vacuum fluorite tube with which it is possible to observe spectra up to 1200 A; and 3) a vacuum monochromator (up to 1300-1400°) with a fluorite optic and a photo-electric set-up.

A beginning has been made in production of attachments for the ISP-51 spectrophotometer with a photomultiplier, an amplifier, and a recording attachment. The IKS-11 and IKS-6 for study in the infrared have also been issued, as well as the spectrophotometers SF-4 and SF-2M. For visual observation the following have been prepared: the SL-10 styloscope, the ST-7 stylometer, a manual spectroscope, and a demonstration outfit; new apparatus for measuring spectrograms have also been turned out.

A number of reports were devoted to photoelectric methods which speed up analysis and make it more accurate. Considerable attention was given to impulse sources of excitation, which have several advantages in a number of applications.

Results of study of the processes which occur in the flame of an excitation source and on the electrodes were given in 15 reports. These processes have received little attention so far, although they have a significant effect on the analytical results; these papers were therefore of exceptional value.

Seventy reports touched upon spectrographic analysis of various products; metals, slags, various mineral raw materials, solutions, natural waters,

electrolytic baths, lubricating oils, etc. Methods for detecting small amounts of contamination in metals of high purity (titanium, vanadium, zinc, antimony) were also described.

Papers on the spectrographic determination of hydrogen and oxygen in metals proved of great interest. Mention must also be made of the application of emission spectrographic analysis in biology and medicine as described in papers devoted to the study of the biological role of micro-elements.

Reports were also heard on the following topics: 1) the contemporary study of radiospectroscopy, and 2) the determination of molecular structure by radiospectroscopy.

The conference enabled many scientists in the field of spectroscopy to exchange views and to get acquainted with new apparatus and methods, new techniques and improvements, so it should prove of great help in ensuring successful continuation of work in this field.

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